THE PHOTO-CHEMISTRY OF SOME CHLORONITROSO COMPOUNDS.

T H E S I S

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by

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Part 1. Historical and Theoretical.

Although it has been known from very early times that light is essential for certain processes such as the growth of plants, it was not until the beginning of the 18th century that any systematic research on photo-chemistry was carried out. The earlier work was chiefly connected with the blackening of silver salts when exposed to the light. Since that time a great deal of work has been done on photo-chemistry, but as the theory of light in favour at this time was the wave theory which did not give any idea of the energy of light, the researches were mostly of a qualitative nature, and no systematic classification of the results was possible. Thus, the earlier workers confined themselves to the study of the laws of absorption and to the measurement of the reaction velocities.

The first important advance in photo-chemistry was made independently by Grotthus in 1817 and Draper in 1841. They enunciated the first law of photo-chemistry which states that only light which is absorbed by the system can bring about any chemical change in it. Light which is transmitted or reflected has no chemical effect.

Although the Grotthus Draper Law is universally true, its converse is not. That is, all the light which is absorbed does not cause chemical change. When light energy

is absorbed by a system it can be used in various ways. Thus it may be converted into thermal energy, be re-emitted as fluorescence, resonance or phosphorescence, or it may cause a chemical change. It is not surprising, therefore, that only a small proportion of the substances which absorb light are decomposed by it.

The Grotthus Draper Law thus necessitates the study of absorption as a preliminary to the study of a photo-chemical problem. The fundamental laws of absorption are those of Lambert and Beer. They can be summarised in the equation

$$\text{Log } \frac{I_0}{I} = \varepsilon cd.$$

where I_0 is the intensity of the incident light, I is the intensity of the emergent light, c is the concentration in gram molecules per litre, d is the thickness in centimetres and ε is the molecular extinction coefficient. The molecular extinction coefficient is equal to the reciprocal of the length in cms. of the column of a molar solution required to reduce the intensity of the incident light to 1/10 of its value.

The methods of measuring extinction coefficients are too well known to be described here. However, it must be emphasised that such measurements are a necessary preliminary to the study of any photo-chemical problem. The number of absorption bands and the extinction coefficients should be measured. Experiments should also be carried out to ascertain which band or bands are photo-chemically

active. The measurement of the absorption spectrum of the chloronitroso compounds studied here is described in the third part of this thesis.

The greatest advance in photo-chemistry was made in 1912 when Einstein applied to it the quantum theory of Planck. Briefly, Planck's theory stated that light is not emitted or absorbed continuously, but as discrete bundles of energy or quanta. The size of the quantum is dependent on the frequency of the radiation and is given by the relation $E = h\nu$

where E is the energy in the quantum in ergs,

h is Planck's constant $6{\cdot}554 \times 10^{-27}$ ergs seconds,

ν is the frequency of the radiation.

Einstein made the generalisation that in a system which is photo-sensitive, the absorption of one quantum of light causes the reaction of one molecule of the substance. That is, the amount of energy (light of frequency ν) required to decompose one gram molecule of the substance is $Nh\nu$ ergs or $\frac{28470}{\lambda \text{microns}}$ cals, where λ is the wave-length of the light.

Since the formulation of Einstein's Law of Photo-chemical Equivalence, many experiments have been carried out to verify its validity. The most famous of these are the classical researches of Warburg in this field.

In general, it has been found that although the law is obeyed in principle, it is not obeyed exactly. Many cases are known in which the absorption of one quantum of energy

is followed by the decomposition of 2, 3 or even as many as 10^6 molecules of the substance. In many other cases the absorption of 2 or more quanta are required to bring about the decomposition of one molecule. The number of molecules of the substance decomposed for each quantum of light absorbed is called the quantum yield or the quantum efficiency. Further, the quantum yield is found in many cases to vary with temperature, concentration, or solvent, whereas, if the Einstein Law were obeyed it would be independent of these factors.

A study of the thermodynamical derivation of Einstein's Law readily explains these discrepancies. The type of photo-chemical change for which the proof holds rigidly is one in which

(1) All reacting molecules are at the same energy level before reacting and are therefore equally reactive.
(2) The reactivity of the absorbing molecules under a given radiation density is independent of temperature.
(3) The amount of energy absorbed by the molecule is the same in every case and is independent of temperature.
(4) The product after the absorption of energy is fundamentally unstable with respect to the original absorbing system, and will revert to the latter spontaneously at a rate independent of temperature.
The whole process is thus identical for all the molecules. (1).

It is seen that these conditions are seldom obeyed. They would be obeyed, however, in the formation of a higher Bohr state of a molecule. That is, the activation of a molecule by light. It is therefore generally concluded that the Einstein Law holds for the primary activation of the molecule only, one activated molecule being formed for each quantum of light absorbed. An activated molecule may then react in any of the following ways.

(1) It may decompose spontaneously or on collision with another molecule. In such a case the Einstein Law would be obeyed.

(2) It may react with an unactivated molecule of the substance with the decomposition of both of them. In this case the quantum yield would be 2.

(3) It may react with an unactivated molecule to give products which initiate a chain reaction. In this case the quantum yield would be much greater than 2, the actual value depending on the length of the chain.

(4) It may collide with a solvent molecule and lose all or some of its excess energy. If only some of the molecules do this while others react as in (1) the quantum yield will be less than 1. Further, the quantum yield will change with concentration as that will vary the probability of such collisions occurring.

(5) It may not have sufficient energy to cause decomposition, but may decompose on absorption of a second

quantum. Again the quantum yield will be smaller than 1.

We thus see that although the Einstein Law does not hold for the complete reaction we can explain the experimental values of the quantum yield by the factors given above if we assume that the law holds for the primary reaction. Further, the effects of temperature, concentration and solvent can also be explained since these factors will influence the rates of the secondary reactions.

If we consider the reasons given above why the quantum yield should differ from unity, we see that the measurement of the quantum efficiency will often give a valuable clue to the elucidation of the mechanism of the reaction. Partly because of this, and partly with a view to verifying the Einstein Law of Photo-chemical Equivalence, many authors have measured the quantum yields of different reactions. A brief review of some of these experiments is given below. As this thesis describes the photo-chemical decomposition of chloronitroso compounds special reference will be made to the few experiments in which compounds containing the nitroso group have been examined.

The earliest and most famous measurements of quantum yields were carried out by Warburg. Indeed, even before the enunciation of the Einstein Law, Warburg was engaged

in measuring the "photochemische ausbeute" or the fraction of the energy absorbed which was used to bring about the chemical reaction. He measured the amount of NH_3 decomposed by a certain amount of light energy and from the heat of formation of NH_3 calculated the fraction of the energy used to bring about decomposition. (2). He carried out similar experiments for the formation of ozone. (3). With the introduction of the Einstein theory these results were recalculated to give the quantum yields and further experiments were carried out. He found values for the quantum yield ranging from 0·11 for the change from maleic to fumaric acid to 2 for the decomposition of HBr, but he was able to explain the deviations from the Einstein Law in every case. The explanation of the reaction mechanism which also explains these deviations are, however, too well known to be recorded here.

Other well known workers in this field are Weigert who measured the quantum yield for the polymerisation of anthracene (4), the change from o-nitrobenzaldehyde to o-nitrosobenzoic acid (5), and the decomposition of AgCl (6); Kistiakowsky who studied the decomposition of NOCl (7), Cl_2O (8), etc. and Eggert who studied several different reactions.

Most of the work on photo-chemistry has been done with ultra violet light or light from the blue end of the visible region. Practically the only work done with

light from the red end of the spectrum is that done on the nitroso compounds described below.

Hoffman investigated the decomposition of β-caryophyllene nitrosite. (9). This compound has a narrow absorption band at 6800A and is decomposed by light of that wave-length. The decomposition products were found to consist of nitrogen, oxides of nitrogen and two nitrosates of caryophyllene. Hoffman also measured the quantum yield for the decomposition. He used Cd or Zn quarts capillary lamps and in some cases tungsten filament lamps as the light source. The light was rendered monochromatic by a Hilger spectrometer. The rate of decomposition was followed by (a) the volume of nitrogen liberated, (b) the bleaching of the blue colour. As the light was not completely absorbed the energy was found by measuring the absorption at frequent intervals from the beginning of the experiment until no absorption occurred. The total energy was then found by a graphical method. The values obtained for the quantum yield were 0·38 for the evolution of nitrogen and 1·3 for the disappearance of the blue colour.

Hoffman suggested the following mechanism:-

$$\beta C_{15}H_{24}N_2O_3 + h\nu = \beta C_{15}H_{24}N_2O_3^{*}$$

$$\beta C_{15}H_{24}N_2O_3^{*} = C_{15}H_{24} + N_2O_3$$

$$\beta C_{15}H_{24}N_2O_3^{*} = \Delta C_{15}H_{24}N_2O_3$$

$$2\ \Delta C_{15}H_{24}N_2O_3 = (C_{15}H_{24}N_2O_3)_2$$

$$(C_{15}H_{24}N_2O_3)_2 + C_{15}H_{24}N_2O_3 = N_2 + C_{15}H_{24} + C_{15}H_{24}N_2O_4 + C_{15}H_{24}N_2O_5$$

The quantum efficiency calculated from the above mechanism would be 0·46 for evolution of nitrogen and 1·46 for the bleaching of the colour.

The technique used for measuring the quantum efficiency described in this paper has several disadvantages. In the first place, the use of a Zn or a Cd lamp with a monochromater as a light source, although advantageous in that it gives a beam which is monochromatic to a high degree, has the great disadvantage that the beam obtained is of very small dimensions and intensity. This necessitates lengthy exposures of the compound and so makes the experiment rather tedious. In addition, if there is any appreciable dark reaction the error due to it will be much greater than if the solution was exposed to an intense beam of light for a shorter time.

Secondly, the light was not completely absorbed by the solution. This made it necessary to measure the amount of absorption at frequent intervals. In addition to making the experimental technique more difficult, it also adds unnecessarily to the difficulty of the calculation of the energy absorbed. If the light is completely absorbed, the total energy supplied is much more easily and more accurately evaluated.

Anderson, Crumpler and Hammick studied the photo-

decomposition of nitroso-isopropyl acetone and βnitroso-βεdimethylhexane. (10). These compounds decompose with a quantum yield of 1 to give hyponitrous acid, together with mesityl oxide in the case of nitroso-isopropyl acetone, and an unsaturated hydrocarbon, probably βεdimethylhexene in the other. The mechanism suggested is:-

$$Me_2C(NO)-CHR + h\nu = \tfrac{1}{2} H_2N_2O_2 + Me_2C=CHR$$

In their quantum yield experiments on nitroso-isopropyl acetone, these authors employed filters which transmitted a band between 6400A and 7100A. The solution was exposed to this light for 13 hours. As the light was not completely absorbed " the amount actually absorbed was found by a difference method ". The amount of decomposition was found by taking measurements of colour density on a Hilger Nutting Spectrophotometer. The quantum yield for βnitrosoβε dimethylhexane was measured by comparing the rate of decomposition with that of nitroso-isopropyl acetone under the same conditions of illumination.

Other experiments showed that the rate of decomposition was proportional to the light intensity, and independent of the concentration of the solution.

The method of measuring quantum yields described in this paper has the same disadvantage as Hoffman's method, namely incomplete absorption of the light. In this case

there is the additional disadvantage that the light was not monochromatic. Further, the measurement of the rate of decomposition was made with a Hilger Nutting Spectrophotometer the accuracy of which would not be very great. Although the photometer reads with an accuracy of 2%, the change in colour density is so small that the resultant error would be fairly large.

Hammick and Lister studied the photo-chemistry of tetramethylethylene nitrosochloride, βchloroβnitroso-γγdimethylbutane, chloronitrosocyclohexane and βnitro-βnitrosopropane in the presence and in the absence of air. (11).

The photolysis of tetramethylethylene nitrosochloride in presence or absence of air gave nitrous acid, nitrogen and tetramethylethylenedichloride. The mechanism is the elimination of HCl as in the compounds described in the previous paper.

βchloroβnitrosoγγdimethylbutane in presence of air was photo-oxidised to the nitro compound. In absence of air practically no photolysis occurred even on prolonged illumination.

Chloronitrosocyclohexane was also photo-oxidised to the chloronitro compound in presence of oxygen. Photolysis also occurred in the absence of oxygen, but the products were gummy materials and could not be identified. Traces of HCl and nitrous acid were detected,

however, In the course of the present work some chloronitrosocyclohexane was prepared and decomposed. It was found that the HCl liberated, instead of being a trace as found by Hammick and Lister, was 96% of the total chlorine in the solution. The same result was obtained using alcohol or ether as solvent.

βγβnitroβnitrosopropane was photo-oxidised to the dinitro compound. In the absence of air, nitrogen was evolved but no other products could be isolated.

The quantum efficiency was measured by the same method as that described by Anderson, Crumpler and Hammick. (15). " Owing to the fact that no colour filters are known that will transmit even approximately monochromatic light at wave-lengths within the range of those absorbed by the nitroso compounds investigated, the only filter used was one to eliminate infra red radiation"

The results of the quantum yield measurements were as follows:-

	Solvent.			
	C_6H_6	$CHCl_3$	MeOH	EtOH
Tetramethylethylene nitrosochloride.	1·04	0·84	1·94	1·87
βchloroβnitroso γγdimethylbutane.	0·91	0·93	1·75	1·56
Chloronitroso cyclohexane.	0·81	----	2·42	2·17
βnitroβnitroso propane.	0·82	0·85	----	----

The quantum yield is given as 1, the high values in alcohol being attributed to solvent effect.

Comparisons of the rate of photolysis at constant illumination in nitrogen, air and oxygen were also made and gave the results:-

		gm.mols/min. x 10^{-5}		
	Solvent.	N_2	Air.	O_2
Tetramethylethylene nitrosochloride.	C_6H_6	1·08	1·04	1·06
	MeOH	2·41	2·41	2·57
βchloroβnitroso γγdimethylbutane.	C_6H_6	0·2	0·87	1·21
	MeOH	0·81	1·67	2·41
Chloronitroso cyclohexane.	MeOH	2·22	3·25	----
βnitroβnitroso propane.	C_6H_6	0·3	0·82	0·89

Since the actual quantum yield of tetramethylethylene nitrosochloride in benzene is 1·08, we can take these figures as the quantum yields under these conditions. An analysis of the results is interesting.

Firstly, the figure for tetramethylethylene nitrosochloride in methyl alcohol is 2·41. This figure does not agree too well with the value 1·94 given in the first table.

Secondly, the quantum yield for βchloroβnitroso-dimethylbutane is 0·8 in the absence of air. This fairly rapid reaction does not agree with the following quotation from the text of the paper. " In absence of air very little photolysis occurs even after prolonged

irradiation ". In the course of our work on chloro-nitroso compounds, some of the above compound was made and it was found that practically no decomposition had taken place even after a week's illumination with strong sunlight if precautions were taken to exclude all air from the solution. It would thus appear that the value 0·8 is incorrect, probably due to the incomplete elimination of air.

Mitchell and Carson in a paper describing the preparation of chloronitrosohexanes by the action of nitrosyl chloride on normal hexane under the influence of light, mention that chloronitrosohexanes are decomposed by red light in the absence of air and that the hydrochlorides of methyl-butyl and ethyl-propyl ketoximes can be isolated from the solution. No further work was done on the decomposition. (12).

The work described in this thesis was carried out with chloro-nitroso compounds of the type $R_1-\overset{NO}{\underset{Cl}{C}}-R_2$ which have a photochemically active absorption band in the red. We became interested in them from the point of view of asymmetric photo-chemical decomposition, that is, the production of rotation from a racemic substance by partial decomposition with circularly polarised light. (13). It was thought that the compounds might be suitable for this purpose and so it was decided to study their photo-chemistry, including the

measurement of the quantum yield.

Since, as we have seen, no satisfactory method of measuring quantum yields with red light has been described it was necessary to develop a technique of our own. The final method adopted is described in a paper which has been published, giving the results of the investigation of the decomposition of βchloroβnitrosobutane by red light in the absence of oxygen. (14).

In the measurement of quantum yields there are four main points to be considered. These are:-

(1) The light source.

(2) Monochromatism.

(3) Measurement of energy.

(4) Measurement of change in concentration.

The Light Source.

The choice of light source depends largely on the spectral region in which the measurements are being carried out, as the source must be capable of giving an intense beam in this region. It is also desirable that the intensity should be as constant as possible so that the energy measurements may be sufficiently accurate. For work in the ultra violet, Warburg made use of the zinc or aluminium spark. (2). For the near ultra violet and the visible with the exception of the red and the yellow, the quartz mercury vapour lamp has been most frequently used. The single lines of this lamp make it

especially suitable for quantum yield measurements. Other sources which have been used in the visible are the tungsten and nitra lamps used by Kistiakowsky in the decomposition of NOCl (7), and the carbon arc used by Bowen and Sharp for the same reaction. (15).

When we consider the red end of the spectrum, we find that the only source which gives an intense red light is the carbon arc. This source does not seem to have been much used in the measurement of quantum yields. It has been used, however, by Bowen and Sharp as described above, and by Taylor in an attempt to decompose NOCl by infra red radiation. (16). The chief reason why it has not been frequently employed is probably because it is very variable. An automatic carbon arc was used in the present work and it was found impossible even by the most careful regulation to keep the intensity any steadier than 10%. However, a complete record of the variations in intensity was kept by means of a photo-cell and a recording galvanometer. In this way the error due to the fluctuations in intensity were eliminated. It is interesting to record that in the decomposition of NOCl, Kistiakowsky used a second thermopile to eliminate errors due to fluctuations in intensity. (7).

Monochromatism.

In all photo-chemical work there are two factors about the light source to be considered, namely, inten-

sity and monochromatism. In most cases these two factors cannot be reconciled so one is obtained at the expense of the other, and as it is desirable to complete the experiment in a reasonable time especially if there is any dark reaction, it is usually the purity of the light which is sacrificed. Thus, although the spectroscope is the most efficient means of obtaining a monochromatic beam, the intensity is so small that it is seldom used. Examples of its use are recorded by Villars (17) for the decomposition of KNO_3 and by Hoffman (9) for the decomposition of caryophyllene nitrosite.

The commonest method of obtaining monochromatic light is by the use of colour filters. These are solutions or glasses which transmit preferentially in certain regions of the spectrum. Special filters which transmit the single colours of the mercury vapour lamp can be obtained commercially and are frequently used.

For work in the red we again find peculiar difficulties. According to Hammick and Lister (11), " no colour filters are known that will transmit even approximately monochromatic light at wave-lengths absorbed by the nitroso compounds investigated ".

To obtain red light for the work described in this thesis, a filter first described by Christiansen (18) was used. It consists of a suspension of powdered glass in methyl benzoate, and transmits light for which the

refractive index of the glass and the methyl benzoate are equal, all the other wave-lengths being scattered. By altering the temperature of the filter a monochromatic beam of any desired wave-length can be obtained. An optical train for the use of such filters has been described by Weigert and his co-workers. (19). (20). (21).

It would appear that the work described in this thesis is the first application of such a filter to the measurement of quantum yields.

Energy Measurements.

The most frequently used method of measuring the amount of energy absorbed by a system is by means of a thermopile and galvanometer. Other methods have been described, however. For example, Riddal and Morrish (22) used a blackened air thermometer filled with aniline. The air thermometer was calibrated by immersing an electrical resistance in the aniline and heating it with a known current and voltage. Daniels (23) in his work in the infra red filled his reaction cell with a 0·4 N cupric chloride solution which absorbs all radiation, and measured the rise in temperature in a given time. He then calculated the energy absorbed by the NOCl from its absorption spectrum and from the spectral distribution of energy of the light source.

When the thermopile and galvanometer are used it is necessary to calibrate them against a standard source of

energy. The standard most frequently used and the one used in this work is the Hefner candle, the total energy from which has been measured by Gerlach. (24). Other methods of calibration are also possible. In America it is possible to obtain standard lamps from the Bureau of Standards and these are very often employed in that country. For the decomposition of NOCl, Bowen and Sharp (15) calibrated their thermopile with the black body radiation from Leslie cubes filled with boiling water and boiling aniline.

Measurement of the Change in Concentration.

The methods of measuring concentration can be divided into Chemical and Physical methods. The chemical methods depend solely on the nature of the compounds being investigated and need not be further dealt with here. A chemical method (the titration of HCl set free) was at first attempted in the present work but had to be abandoned as it did not give constant results.

Examples of physical methods which have been used are :-

(1) Conductivity (Weigert and Brodman). (5).

(2) Potentiometer. (Rideal and Norrish). (22).

(3) Light absorption. (Hammick. (10). Weigert. (4). Rideal and Norrish (22). etc.)

Of the three methods, the third is the most important. For the actual measurements, Hammick and his

co-workers and also Rideal and Norrish employed a Hilger Nutting Spectrophotometer, the disadvantages of which have been already discussed. Weigert measured the absorption with a thermopile and the mercury vapour lamp. Although this is an improvement on the visual method, it suffers from the fact that the light is not quite steady and also from the fact that the zero of the thermopile changes. For the present work, Weigert's method was improved by substituting for the mercury vapour lamp, a light source which was steady to 1 part in 500 (filament lamp run off cells), and using a photo-cell instead of a thermopile.

To recapitulate briefly, the main features of the method developed for measuring quantum yields in red light are as follows:-

The light source is a carbon arc which gives an intense though somewhat unsteady beam. The variations in intensity are recorded with a photo-cell and recording galvanometer. The light is rendered monochromatic by means of a Christiansen filter.

The amount of energy absorbed is measured by means of a thermopile and galvanometer previously calibrated against a Hefner lamp.

The amount of decomposition is found by measuring the change in light absorption by means of a steady light source and a photo-electric cell.

THE PHOTOCHEMISTRY OF SOME CHLORONITROSO COMPOUNDS.

Part 2. - The Decomposition Products.

The compounds whose photo-chemical decomposition was studied were chloronitroso compounds of the type $R_1-\overset{\overset{NO}{|}}{\underset{\underset{Cl}{|}}{C}}-R_2$ where R_1 and R_2 are simple alkyl radicals. These compounds were made by Rheinbold and Dewald (25) by the action of nitrosyl chloride on the corresponding oxime thus:-

$$R_1-\overset{\overset{NOH}{|}}{C}-R_2 \;+\; 2NOCl \;=\; R_1-\overset{\overset{NO}{|}}{\underset{\underset{Cl}{|}}{C}}-R_2 \;+\; HCl \;+\; 2NO$$

Mitchell and Carson obtained chloronitrosohexanes by the action of nitrosyl chloride on n hexane under the influence of light. (12). This reaction is essentially the same as that above, as the first stages of the reaction are:-

$$C_6H_{14} + NOCl = C_3H_7-\overset{\overset{NO}{|}}{\underset{\underset{H}{|}}{C}}-C_2H_5 + HCl = C_3H_7-\overset{\overset{NOH}{|}}{C}-C_2H_5 + HCl$$

The compounds can also be obtained by the action of chlorine on the oxime. This was the method which was used for the preparation of the compounds used in this work.

$$R_1-\overset{\overset{NOH}{|}}{C}-R_2 \;+\; Cl_2 \;=\; R_1-\overset{\overset{NO}{|}}{\underset{\underset{Cl}{|}}{C}}-R_2 \;+\; HCl$$

100 gms. of the ketoxime were dissolved in 300 ccs. of water containing sufficient HCl to dissolve the oxime.

The solution was placed in a freezing mixture and a rapid stream of chlorine was passed into it. A violet blue liquid separated out on the top of the solution. When no more liquid separated the top layer was removed, washed with dilute sodium carbonate till free of acid, and then with water. It was then dried over anhydrous sodium sulphate and distilled under reduced pressure. The three compounds investigated had the following constants.

	$CH_3-\overset{\overset{NO}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3$	$CH_3-\overset{\overset{NO}{|}}{\underset{\underset{Cl}{|}}{C}}-C_2H_5$	$CH_3-\overset{\overset{NO}{|}}{\underset{\underset{Cl}{|}}{C}}-C_4H_9$
B.Pt.	35°C/200mm.	36°C/63mm.	39°C/11mm.
Cl. (Stepanow's method)	32·9%	29·1%	23·7%
Cl. (Calculated)	33·0%	29·2%	23·7%

The compounds have an absorption band associated with the nitroso group in the red end of the spectrum. (See Part 3 of this thesis.) They are decomposed by light within the band, both in the presence and in the absence of oxygen.

Mitchell and Carson found that when chloronitrosohexanes were decomposed by red light in the absence of oxygen, the corresponding oxime hydrochlorides could be isolated from the decomposed solution. (12). They did not carry out any further work on the subject, however.

In this thesis there is described a detailed inves-

tigation of the photo-chemical decomposition of some of these compounds, both in the presence and in the absence of oxygen.

Decomposition of ßchloroßnitrosobutane in the absence of oxygen.

The decomposition was mainly carried out in methyl alcohol solution, although experiments carried out with other solvents will be described later. Methyl alcohol was chosen as solvent because the decomposition products were soluble in it, and so the solution remained homogeneous throughout the experiment. When hexane or carbon tetrachloride were used, the decomposition products separated out as an oil and were much more difficult to work up. The concentration of the solution was 5% as this gave a product that was almost colourless. If a more concentrated solution was used the solution became brown during the decomposition.

The solution was contained in sealed glass tubes to prevent photo-oxidation. They were placed in a glass tank in which cold water was circulated and were illuminated by six metal filament lamps surrounding the tank. The lamps were surrounded with aluminium foil to act as a reflector. On exposure to the light, the solution became green and then faintly yellow. On standing the yellow colour deepened to brown. The tubes were now

opened and the solution was found to be strongly acid. The acid was identified as HCl. It was estimated by decomposing a solution of chloronitrosobutane of known strength and titrating the resulting solution with standard silver nitrate or standard alkali. Both methods were used and gave identical results. The actual value of the amount of HCl was not absolutely constant but varied between 90% and 95%.

The methyl alcohol was removed from the decomposed solution by evaporation under reduced pressure, keeping the temperature below 20°C. A brown oil was left which it was later discovered, went solid when the last traces of alcohol were removed on an oil pump. The brown oil was dissolved in a little water and neutralised with a 30% solution of caustic potash. When the solution was neutral a little brown oil separated. The oil was extracted with ether, the ether dried over sodium sulphate and distilled under reduced pressure. In the preliminary experiments the liquid was distilled at 20mm. In this case a small amount of a colourless liquid B.Pt. 70°/20mm was obtained. A considerable amount of charring took place and no other products were obtained. The liquid had the characteristic smell of methyl ethyl ketoxime and gave n_D^{25} 1·4405. Methyl ethyl ketoxime gave n_D^{25} 1·4410. A little of the liquid was steam distilled with dilute HCl. The distillate was buffered with

sodium acetate and semicarbazide hydrochloride added. White crystals separated on shaking. After recrystallisation from alcohol they melted at 143°C. A sample of the semicarbazone made from methyl ethyl ketone also melted at 143°C, and a mixed melting point showed no depression. The liquid was thus definitely identified as methyl ethyl ketoxime. About 1gm. of methyl ethyl ketoxime was obtained from 10gms. of chloronitrosobutane.

It was desired to know how much methyl ethyl ketoxime was formed in the decomposition, so attempts were made to estimate it.

The first method used was to allow the decomposed solution to stand in order to hydrolyse the oxime to the ketone. The ketone was then precipitated as the 2-4-dinitrophenylhydrazone and weighed. The method was not very successful as the precipitation was not quantitative.

The second and more satisfactory method depended on the formation of the blue chloronitrosobutane by the action of chlorine. A solution of known strength was decomposed and a stream of chlorine passed into the solution till no increase in the blue colour occurred. A solution of oxime in methyl alcohol of a strength corresponding to the theoretical amount of oxime in the decomposed solution was treated in the same way. The two

solutions were then matched in a colorimeter. Owing to the presence of the yellow colour due to dissolved chlorine, it was necessary to use a red screen to make matching possible. The results obtained indicated a yield of methyl ethyl ketoxime of approximately 20% of the theoretical amount.

As the production of methyl ethyl ketoxime and HCl from chloronitrosobutane requires the addition of two hydrogen atoms according to the equation

$$CH_3CH_2C(NO.Cl)CH_3 + 2H = CH_3CH_2C(:NOH)CH_3 + HCl$$

it was thought that these might be obtained from the methyl alcohol. This seemed to be supported by the fact that when the decomposition was carried out in methyl alcohol, a solvent which would readily lose hydrogen, the solution remained homogeneous and almost colourless. If the solvent was a substance like hexane or benzene which does not readily part with hydrogen, the products separated as a brown oil and a considerable amount of charring took place. If the two hydrogen atoms were obtained from the methyl alcohol one would expect to get formaldehyde formed. An exhaustive search for formaldehyde was thus carried out but no formaldehyde could be detected. The solution did reduce ammoniacal silver nitrate but this was attributed to the presence of hydroxylamine hydrochloride formed by the hydrolysis of methyl ethyl ketoxime. This was confirmed by the failure of

the solution to give a precipitate with dimedone which is a specific test for aldehydes. Attempts to detect the presence of condensation products of formaldehyde were also unsuccessful. Further, no gaseous products could be detected in the decomposition so that the oxidation of the alcohol could not have proceeded to a further stage.

Hammick (10) studied the decomposition of nitrosoisopropyl acetone and some other compounds and obtained hyponitrous acid and nitrous acid in the solution. Tests were therefore carried out on the solution of decomposed chloronitrosobutane to see if these acids could be detected. Tests for hyponitrous, nitrous and nitric acids were all negative. This suggests that in this reaction the nitrogen is never separated from the carbon atom to which it is attached. If it were separated and then added on at a later stage one would expect to find traces of the oxides of nitrogen or the corresponding acids.

Since, as we have seen above, the absence of formaldehyde indicates that the chloronitrosobutane does not get the two hydrogen atoms necessary for the production of methyl ethyl ketoxime from the methyl alcohol, it must get them from another molecule of chloronitrosobutane. Further evidence of this is the fact that the compound decomposes in carbon tetrachloride solution

and methyl ethyl ketoxime can be isolated from the solution (vide infra). In that case there must be some other product formed in the reaction. It was decided to attempt the isolation of this compound. A considerable amount of difficulty was anticipated as it was expected that the compound would be unsaturated and probably very unstable.

When an alcoholic solution of chloronitrosobutane was decomposed by light and the decomposed solution allowed to stand in an open beaker for about two weeks, a small quantity of a brownish solid separated out. The solid was removed and examined. It was found to be almost insoluble in water. It was, however, soluble in acids or alkali, but was reprecipitated on neutralisation. It was obtained in a much purer state by dissolving in caustic soda and precipitation with HCl. It was then finally purified by recrystallisation from absolute alcohol. It melted and sublimed at 234°C. On analysis it gave N 23·6%. As it gave a red precipitate with a nickel salt it was suspected to be dimethyl glyoxime.(melts and sublimes at 234°C. N 23·6%). An acetyl derivative was prepared by boiling with acetic anhydride. It melted at 110°C, the same melting point as the acetyl derivative made from a sample of dimethyl glyoxime. A mixed melting point showed no depression. The yield of dimethyl glyoxime was very poor, only about 1gm. being obtained

from 50gms. of chloronitrosobutane.

It was thought that the dimethyl glyoxime was not formed during the photo-chemical decomposition, but was formed subsequent to it, by products of the decomposition. This was substantiated by the fact that no dimethyl glyoxime separated out when the alcohol was removed in vacuo, immediately after the decomposition. To prove whether dimethyl glyoxime was present at the end of the photolysis or not the following experiment was carried out. A little of the decomposed solution was dissolved in water and added to a solution of a nickel salt. The solution was then made just alkaline with ammonia. If dimethyl glyoxime is present a red precipitate should be obtained. In the experiment no precipitate was obtained. This proves that dimethyl glyoxime is not itself a product of the photolysis but is formed by the interaction of other reaction products. Also, since it only develops slowly it is likely that one of the compounds necessary for its formation is only produced slowly by the decomposition of a second substance. It had previously been noticed that when methyl ethyl ketoxime is allowed to stand with HCl in methyl alcohol, hydroxylamine hydrochloride is slowly deposited. It was thus thought that dimethyl glyoxime was formed by the action of hydroxylamine hydrochloride on some other compound. A freshly decomposed solution of chloronitrosobutane was therefore

dissolved in water and hydroxylamine hydrochloride added. The solution was then added to a nickel solution and made just alkaline with ammonia. A copious red precipitate was obtained, showing the presence of dimethyl glyoxime. A blank test with the hydroxylamine hydrochloride omitted gave no precipitate.

It was decided to estimate the amount of the parent of dimethyl glyoxime which was present. The following method was used. A solution of chloronitrosobutane of known strength was decomposed by light. A measured volume of this solution was dissolved in water and treated with an excess of hydroxylamine hydrochloride and allowed to stand for a day. An excess of a nickel solution was then added and the whole made faintly alkaline with ammonia. The red precipitate of the nickel complex was filtered, washed, dried at 110°C and weighed. 10ccs. of a 4·087% solution when treated this way gave a precipitate weighing 0·0546gms. This corresponds to a 11·15% yield of the parent of dimethyl glyoxime. It has to be remembered, however, that this figure is a minimum value. The actual amount may well be much more than this, due to the fact that the action of hydroxylamine hydrochloride on the compound may not be quantitative.

Since we have now proved the presence of a product other than methyl ethyl ketoxime, it became necessary to isolate it. This problem presented some difficulty owing

to the presence of HCl. When the decomposition product was evaporated and the resulting oily mass dissolved in water and neutralised, a small amount of oil separated. This, on distillation, gave methyl ethyl ketoxime. No other product could be isolated, however, because as soon as the temperature was raised above 100°C charring took place. Thus, as soon as most of the oxime was removed, the whole mass charred and only carbonaceous matter was left in the flask. At first this was attributed to the presence of traces of HCl which had not been completely removed during the process of neutralisation. Attempts were made to eliminate it by prolonged shaking of the solution with dilute sodium carbonate, but charring still took place. It thus became apparent that we must seek some other explanation. The most natural assumption was that the charring was due to the thermal decomposition of one of the products of the decomposition. It was thought that distillation of the oil at a lower pressure might eliminate the charring. A distillation of the neutral oil was therefore carried out at a pressure of 6mm. In this case, in addition to the small amount of methyl ethyl ketoxime usually obtained, a small amount of a white solid distilled over and solidified in the upper part of the condenser. It was a rather waxy white solid, very soluble in water, alcohol, acetone, ether, etc., but not very soluble in petroleum ether from which it was

recrystallised. It separated as glistening plates M.Pt. 74·5°C after two recrystallisations. The melting point was not raised by further recrystallisation.

A complete analysis gave the following data:-

C 47·8% H 6·7% N 14·0%.

On treatment with hydroxylamine hydrochloride the solid gave dimethyl glyoxime M.Pt. 234°C. The solid is therefore the one which gives rise to dimethyl glyoxime when the decomposed solution is allowed to stand. The formation of dimethyl glyoxime by the action of hdroxylamine hydrochloride, together with the analysis is sufficient to identify the compound as the monoxime of diacetyl which has

C 47·5% H 6·9% N 13·9% M.Pt. 74·5°C.

It has been shown that when the decomposed solution is evaporated under reduced pressure, neutralised, extracted with ether and the ether distilled at a pressure of 6mm, methyl ethyl ketoxime and diacetyl monoxime are obtained. From 10gms. of chloronitrosobutane about 1gm. of oxime and 0·3gms. of diacetyl monoxime were obtained. In addition, only a very small amount of an oily residue was left behind in the distilling flask. It is thus apparent that a very large proportion of the decomposition products had been lost during the processes described above. An attempt was made to trace at which stage of the procedure this loss occurred.

10gms. of chloronitrosobutane were decomposed by light in methyl alcohol solution. The methyl alcohol was evaporated off under reduced pressure and a semi-solid mass was obtained. This product was weighed. It was found that when allowance was made for the HCl which had been carried over with the alcohol, the solid accounted for the whole of the chloronitrosobutane. The solid was dissolved in water, neutralised and extracted with ether. The ether extract was distilled as before and gave 1gm. of methyl ethyl ketoxime and 0·2gms. of diacetyl monoxime. About 1gm. of an oily residue was left in the flask. This experiment showed that the loss occurred between the addition of the semi-solid mass to water in order to neutralise it and the extraction with ether after neutralisation. It was then apparent that there must be a large amount of the decomposition product which is not extracted with ether, but remains dissolved in the water. To isolate this material the following method was used.

The semi-solid mass obtained by the evaporation of the alcohol from the decomposed solution was dissolved in water and neutralised. The neutral solution was extracted with ether to remove the methyl ethyl ketoxime. The aqueous solution was evaporated to dryness under reduced pressure. The temperature was kept below 40°C to lessen the risk of decomposition. The solid mass which was left

in the flask, and which consisted mostly of potassium chloride was ground up and extracted with ether in a Soxhlet extracter for several hours. A light yellow oil was extracted from the solid. When the oil was cooled and scratched it solidified to a yellowish solid. The solid was recrystallised from ether from which it separated in the form of long white needles. After two recrystallisations it melted at 55°C. Further recrystallisation did not raise the melting point further. The solid was very soluble in water, alcohol, benzene, acetone and most organic solvents. It was only very slightly soluble in ether. This readily explains why it was not extracted with ether but remained dissolved in the water.

A complete analysis of the compound was carried out and gave the following data:-

C 51·3% H 8·5% N 15·2%.

This corresponds to the empirical formula $C_8H_{16}N_2O_3$ which requires the following:-

C 51·1% H 8·6% N 14·9%.

The molecular weight of the compound was determined in benzene by the depression of the freezing point. The result obtained was 235 while $C_8H_{16}N_2O_3$ requires 188. The high result was attributed to association. The molecular weight was also determined in ethyl alcohol by the elevation of the boiling point, using Menzies' improved method involving the use of the differential ther-

mometer. (26). The value obtained was 187 which is in excellent agreement with the theoretical value of 188.

A Zerewitinoff estimation (27) of the number of OH groups in the compound was carried out. 0.0990gm. of the compound caused the liberation of 38.9ccs. of methane. This corresponds to 3 OH groups in each molecule of the compound. (The actual value was 3.1).

It was thought that the compound might be an oxime and so the following experiment was carried out to see if that view was justified. A little of the compound was boiled with dilute HCl for a few minutes. The solution was then treated with a solution of 2-4-dinitrophenylhydrazine. If the compound were an oxime it would be hydrolysed to the ketone and give a derivative with the 2-4-dinitrophenylhydrazine. In the experiment a precipitate was obtained. When the process of boiling with HCl was omitted no precipitate was obtained. It was felt, however, that the experiment was not altogether satisfactory, as in the absence of any knowledge as to the constitution of the compound, it was difficult to say what changes may have been caused by the boiling with HCl. This process may well have caused the compound to undergo a much more profound decomposition, with the consequent production of ketone. As diacetyl monoxime and methyl ethyl ketoxime occur in the decomposition of chloronitrosobutane, it was decided to see if they were

the ketones which were giving the precipitates obtained in the experiment described above. A little of the compound $C_8H_{16}N_2O_3$ was boiled for a few minutes with dilute HCl. To the solution was then added a few crystals of hydroxylamine hydrochloride and a few ccs. of a nickel solution. The solution was made just alkaline with ammonia, when a bulky red precipitate was obtained. It it thus apparent that the HCl does cause a much more profound change than the simple hydrolysis of oxime to ketone, and that one of the products of the change is diacetyl monoxime. In order to see if methyl ethyl ketoxime was another product of this change, a little of the compound was boiled with dilute HCl and a stream of chlorine passed into the solution. A slight blue colour was obtained. As neither the original compound $C_8H_{16}N_2O_3$ nor diacetyl monoxime give a blue colour with chlorine, this is strong evidence for the presence of another oxime. Since $C_8H_{16}N_2O_3$ decomposes on boiling with HCl to give diacetyl monoxime and, presumably, methyl ethyl ketoxime it was thought very probable that it was the source of these compounds obtained in the decomposition of chloronitrosobutane. To prove the actual production of these two compounds from $C_8H_{16}N_2O_3$ it was decided to isolate them. It was also decided to see if they could be produced under the conditions occurring in the solution of the decomposed chloronitrosobutane, that is, on standing

in methyl alcohol with hydrogen chloride.

A solution of hydrogen chloride was made up in methyl alcohol by passing dry HCl into the alcohol. The solution was made up to 4% HCl. To 100ccs. of the solution was added 5gms. of the compound $C_8H_{16}N_2O_3$ and the whole allowed to stand for 24 hours. The methyl alcohol was evaporated off under reduced pressure at room temperature. The residue was dissolved in water and neutralised with 30% caustic potash. The solution was extracted with ether and the ether extract after drying over anhydrous sodium sulphate was distilled at a pressure of 6mm. About 1gm. of a liquid B.Pt. 45°C/6mm. was obtained. It was identified as methyl ethyl ketoxime by its refractive index and the melting point of the semicarbazone prepared from it. In addition about 1gm. of a white solid distilled over and solidified in the upper part of the condenser. Its melting point after recrystallisation from petroleum ether was 74·8°C. A mixed melting point with diacetyl monoxime showed no depression.

It would thus seem that the compound $C_8H_{16}N_2O_3$ is the main product of the decomposition of chloronitrosobutane, and that methyl ethyl ketoxime and diacetyl monoxime are formed from it by the action of an alcoholic solution of HCl. We may now try to write an empirical equation for the reaction. Since the formula for chloronitrosobutane is C_4H_8NOCl, we see that to get 1 molecule

of $C_8H_{16}N_2O_3$ and 2 molecules of HCl from 2 molecules of chloronitrosobutane, we need the addition of 2 hydrogen atoms and 1 oxygen atom. The most obvious way of obtaining these is from water, and the equation may be written

$$2\ C_4H_9NOCl + H_2O = C_8H_{16}N_2O_3 + 2\ HCl.$$

Since there is no water present in the first stages of the reaction, as the decomposition is carried out in methyl alcohol solution, it was thought that the water was only added on when the semi-solid mass was added to water to neutralise it. It was at first thought that the addition of water might be a simple hydration, that is, the compound contained one molecule of water of crystallisation. This theory was not borne out by the facts, as all attempts to dehydrate the compound were unsuccessful.

We must now conclude that the compound $C_8H_{16}N_2O_3$ is not the primary product of the decomposition of chloronitrosobutane by red light, but is a secondary product formed by the action of water on some other product which may be the primary product. It was decided to investigate the possibility of isolating this product in order to verify our deductions. It seemed likely that the semi-solid mass obtained by evaporation of the alcohol from the decomposed solution would contain a large proportion of the product.

A solution of chloronitrosobutane was made up in methyl alcohol and decomposed in the usual way. The methyl alcohol was removed from the solution under reduced pressure, great care being taken to keep the temperature below 20°C. The last traces of methyl alcohol were removed on a dyvac pump. In this way the residue went completely solid and was brown in colour. If the solution used was more dilute and the decomposition was carried out rapidly by having the solution in narrow tubes and exposing them to a very strong light, the solid obtained was not nearly so brown and was much purer than if the decomposition was carried out in the usual way.

As the solid readily absorbed moisture from the air and became wet on standing, great care had to be taken to keep it dry. The solid was washed with methyl acetate which removed most of the brown colour and left a product which was only faintly brown, but which was still largely contaminated with HCl. The solid was very soluble in water, alcohol and acetone. It was insoluble in all other organic solvents except benzene in which it was slightly soluble on heating. It was recrystallised from benzene from which it separated in nacreous plates. It did not give a sharp melting point, but turned red and began to decompose at 110°C.

A weighed amount of the solid was dissolved in water

and titrated with silver nitrate. The titration showed the presence of 17% Cl. A second recrystallisation from benzene did not alter this value. The total chlorine was estimated by Stepanow's method and gave a value of 16·9% Cl. A nitrogen estimation was carried out on the compound and gave the value 13·6% N. As the compound was exceedingly hydroscopic, a carbon and hydrogen estimation was not attempted. The figures obtained for the chlorine and nitrogen estimations, however, agree with the empirical formula $C_8H_{15}N_2O_2Cl$. The latter formula requires N 13·5% and Cl 17·1%. The chlorine is readily replaced as it can be titrated with silver nitrate or alkali.

The isolation of this compound establishes the fact that there is present a compound which would readily give the compound $C_8H_{16}N_2O_3$ by the replacement of Cl by OH, a reaction which seems to take place readily for this compound. The actual production of $C_8H_{16}N_2O_3$ from $C_8H_{15}N_2O_2Cl$ was demonstrated in the following manner.

5 gms. of the compound $C_8H_{15}N_2O_2Cl$ were dissolved in water and neutralised with 30% caustic potash. The solution was evaporated to dryness under reduced pressure at room temperature. The resulting solid was ground up and extracted in a Soxhlet with ether. A yellow oil was extracted. The oil on cooling and scratching solidified to a yellow solid. The solid, after recrystallisation

from ether, melted at 55°C. A mixed melting point with $C_8H_{16}N_2O_3$ was also 55°C. The yield of $C_8H_{16}N_2O_3$ was 2⅛gms.

It has been shown that methyl ethyl ketoxime and diacetyl monoxime are obtained when the compound $C_8H_{16}N_2O_3$ is allowed to stand with alcoholic HCl. Since, however, this compound is formed only on the addition of water and subsequent neutralisation, it would appear that this is not the source of the methyl ethyl ketoxime and diacetyl monoxime isolated from the decomposition products. It now becomes important to know if these two products can be obtained from the compound $C_8H_{15}N_2O_2Cl$.

5gms. of the compound $C_8H_{15}N_2O_2Cl$ were dissolved in 100ccs. of methyl alcohol which had had dry HCl passed into it till it contained 5%. The solution was allowed to stand for 24 hours, and then the methyl alcohol was removed under reduced pressure at room temperature. The semi-solid mass which was left behind was dissolved in water and neutralised with 30% caustic potash. The aqueous solution was extracted with ether, the ether extract dried over anhydrous sodium sulphate and distilled at a pressure of 6mm. 2gms. of methyl ethyl ketoxime and 0.3gms. of diacetyl monoxime were obtained. These proportions are approximately the same as that in which these two compounds are obtained from the photochemical decomposition.

At first sight it seems peculiar that methyl ethyl

ketoxime and diacetyl monoxime should be formed from $C_8H_{15}N_2O_2Cl$ by the action of HCl, as it would require the addition of the elements of water to do so. The explanation probably is that the methyl alcoholic HCl absorbs sufficient moisture from the air to convert at least some of the $C_8H_{15}N_2O_2Cl$ to $C_8H_{16}N_2O_3$ which then splits up into methyl ethyl ketoxime and diacetyl monoxime. The most important fact is, however, that it has been shown that the methyl ethyl ketoxime and diacetyl monoxime isolated in the photo-chemical decomposition could be formed from the compound $C_8H_{15}N_2O_2Cl$ under the conditions which occur in the actual decomposition by light.

It has thus been proved that the compound $C_8H_{15}N_2O_2Cl$ is the main product of the decomposition of chloronitrosobutane by red light in the absence of air. All other products which have been isolated are merely products derived from the decomposition of $C_8H_{15}N_2O_2Cl$, which is a rather unstable substance.

In order to find out how much of the chloronitrosobutane could be accounted for by the decomposition products described, the following experiment was carried out. 80gms. of chloronitrosobutane were dissolved in methyl alcohol and decomposed by light. The decomposition products were worked up by the methods already described. As the compound $C_8H_{16}N_2O_2Cl$ occurs in a very

impure state and great losses occur when it is purified, it was not isolated. Instead, the compound was neutralised and the hydrated compound $C_8H_{16}N_2O_3$ was isolated. The following amounts of the various products were obtained.

Product.	Yield.	%age theoretical.
Hydrochloric acid.	14·5gms.	90%.
Methyl ethyl ketoxime.	7gms.	19%.
Diacetyl monoxime.	1gm.	3%.
$C_8H_{16}N_2O_3$.	17gms.	44%.
Oil (mostly dimethyl glyoxime).	1gm.	---
TOTAL.	40·5gms.	73%.

The reaction products we have isolated therefore account for over 70% of the original chloronitrosobutane. Besides these decomposition products, there is some oil left clinging to the potassium chloride after all the $C_8H_{16}N_2O_3$ has been extracted from it. This oil was obtained by extraction of the potassium chloride with alcohol and evaporation of the alcohol. It was a dark brown, almost black oil, and as it could not be crystallised or distilled even in high vacuo it was not investigated further.

In order to find out if the solvent played any part in the decomposition of chloronitrosobutane, it was decided to investigate the decomposition in acetone,

hexane and carbon tetrachloride. If the solvent plays no part in the decomposition, the same decomposition products should be isolated from all solvents. If on the other hand, the solvent does enter into the reaction, the decomposition products should be different in the different solvents. The results of the investigation are given below.

Decomposition in Acetone.

For the decomposition of βchloroβnitrosobutane in acetone, a 5% solution was again used. The decomposition was carried out exactly as in methyl alcohol. In this case also the solution remained homogeneous and almost colourless. If the solution was allowed to stand, even for a short time after the decomposition was complete, however, it became dark brown in colour. After complete decomposition, the amount of HCl was estimated by titration with standard alkali. 5ccs. of a 5·086% solution of chloronitrosobutane in acetone after decomposition required 20ccs. of a 0·09478 N $Ba(OH)_2$ solution for neutralisation. This corresponds to 89·1% of the total chlorine present. From the remainder of the solution the acetone was evaporated in vacuo. A dark brown semi-solid mass was obtained. The solid was dissolved in water and neutralised. The neutral solution was extracted with ether and on distillation of the ether extract,

in high vacuo, methyl ethyl ketoxime and diacetyl monoxime were obtained. These were identified by their refractive index and melting point respectively. On evaporation of the aqueous layer and extraction of the residue with ether in a Soxhlet, the compound $C_8H_{16}N_2O_3$ was obtained and identified by its melting point and mixed melting point.

It is thus apparent that the decomposition products are the same in acetone and methyl alcohol.

Decomposition in Hexane.

The strength of the solution used and the method of decomposition was the same as before. In this case the solution did not remain homogeneous, but the decomposition products separated out as an oil on the sides and bottom of the tubes. The oil was yellow when it first separated, but became dark brown and then black on standing. The oil was separated off and the hexane washed with water. The washings were added to the oil and the whole neutralised. On extraction with ether and distillation in vacuo, methyl ethyl ketoxime and diacetyl monoxime were obtained. The aqueous layer on evaporation and extraction with ether, yielded a brown oil. On standing for a long time, this oil deposited crystals of $C_8H_{16}N_2O_3$. The oil evidently consists of $C_8H_{16}N_2O_3$ in an impure state. When some of the acid oil was allowed

to stand in water overnight, dimethyl glyoxime separated.

The products of the decomposition are again the same in this solvent. Much more blackening of the products occurs, however. This is due to the fact that the products, being hydrochlorides of oximes, are insoluble in hexane and separate out as an oil. The concentration of HCl in contact with the products is thus much greater than when the solution is homogeneous.

Decomposition in Carbon Tetrachloride.

Carbon tetrachloride was used as solvent because it was certain that it could not contribute anything, apart from chlorine, to the decomposition products. As none of the decomposition products, apart from HCl (either free or in the form of oxime hydrochloride), contained chlorine, it was felt unlikely that the solvent would play any part in the reaction in this case. In this experiment also, the products separated out as an oil at the top of the tubes. The oil was first yellow but soon darkened. On neutralising the oil and working up the products as for the other solvents, methyl ethyl ketoxime, diacetyl monoxime, dimethyl glyoxime and the compound $C_8H_{16}N_2O_3$ were all obtained.

The result of these experiments with the solvents described above prove beyond all doubt that the solvent plays no part in the decomposition of chloronitrosobutane by red light in the absence of oxygen. That is, there is

no interaction between the chloronitrosobutane and the solvent molecules, and hence the solvent contributes nothing towards the decomposition products. The influence of the solvent on the rate of the decomposition will be discussed in Part 3 of this thesis.

It now becomes necessary to ascribe a structural formula to the compounds $C_8H_{16}N_2O_3$ and $C_8H_{15}N_2O_2Cl$, and to formulate the mechanism for the photo-chemical decomposition. The quantum yield was found to be 1·2 which can be regarded as 1 for the present purpose (see Part 3 of this thesis) and so the reaction mechanism must satisfy the three conditions.

(1) It must have a quantum yield of 1.

(2) It must give the products described.

(3) It must be independent of solvent.

Structure of $C_8H_{16}N_2O_3$.

If we consider the compound $C_8H_{16}N_2O_3$ we know it has the following properties.

(1) It has the empirical formula $C_8H_{16}N_2O_3$.

(2) It has 3 OH groups in each molecule.

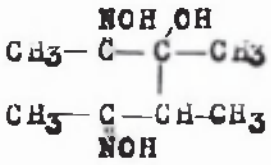
(3) On standing with HCl it decomposes into methyl ethyl ketoxime and diacetyl monoxime.

(4) It is formed by the addition of H_2O to $C_8H_{15}N_2O_2Cl$.

The most striking feature of the compound is the decomposition with HCl. In it we see

$C_8H_{16}N_2O_3$ = C_4H_9NO methyl ethyl ketoxime. + C_4H_7NO diacetyl monoxime.

That is, in the decomposition there is neither the addition nor the elimination of any atom or radical. It is thus very probable that the reaction is a rearrangement of the molecule, with splitting of a bond. The two decomposition products are oximes, that is, they have one hydroxyl group each, and since the original compound had three hydroxyl groups, it is justifiable to assume that in the original compound, two of the hydroxyl groups were attached to nitrogen and the third was attached to carbon. It is also evident then that the rearrangement which occurs involves the third OH group, since it is not present in either of the decomposition products. It is also certain that this rearrangement is the change from C-OH to C=O as the remaining O atom is attached in that manner in diacetyl monoxime. The position of the C OH group is also fixed by its position in diacetyl monoxime. It is attached to the carbon atom adjacent to the oxime group. It is also probable that the two halves of the molecule are attached by the carbon atoms adjacent to the oxime groups. The structural formula suggested for the compound is thus that of αhydroxy$\gamma\delta$dimethylhexan $\beta\varepsilon$dionedioxime.



The rearrangement with HCl

is a simple enol-keto transformation with splitting of the chain, of the type described by Koelichen for diacetone alcohol. (28).

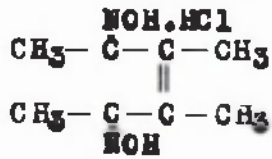
Structure of $C_8H_{15}N_2O_2Cl$.

Since the compound $C_8H_{16}N_2O_3$ is obtained from $C_8H_{15}N_2O_2Cl$ by the addition of water and neutralisation, it is very probable that their structural formulae will be very similar. There are two ways in which the addition of water could occur, namely

(1) Addition at a double bond.

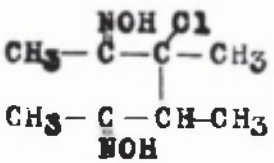
(2) Replacement of Cl by OH.

The two formulae of $C_8H_{15}N_2O_2Cl$ corresponding to these methods would be:-



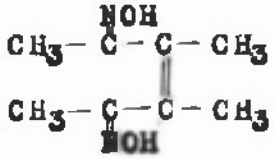
(1)

and



(2)

The first formula is preferred because of the ease with which the Cl is replaced on neutralisation. It is felt that in formula (2) it would not be so easily replaced. It was found to be impossible to test the compound for unsaturation due to the presence of the oxime groups. It is of relatively small importance, however, from the point of view of the mechanism of the photo-chemical decomposition which formula is adopted, as it is almost certain that the compound first formed is $\gamma\delta$dimethyl Δ^{α} hexadiene $\beta\varepsilon$ dionedioxime,



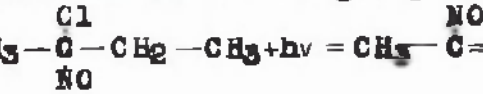
which then adds on HCl either as a monohydrochloride of the dioxime or at the double bond.

The Mechanism of the Reaction.

Anderson, Crumpler and Hammick (15) studied the decomposition of nitrosoisopropyl acetone and suggested the mechanism that NO and H split off from adjacent C atoms, giving hyponitrous acid and an unsaturated compound. In the case of chloronitrosobutane, whose decomposition has been described in this work, since no oxides of nitrogen or the corresponding acids could be detected, it is probable that the bond between the C and N atoms is never broken, but nevertheless, a mechanism can be given which will still be in agreement with, and extend the

mechanism given above.

If we imagine that the first process after activation is the splitting off of a proton from the carbon atom adjacent to the nitroso group, then in the case of nitrosoisopropyl acetone, this is followed by the elimination of the negative ion NO^- with the formation of hyponitrous acid. In the case of chloronitrosobutane the primary process is again the splitting off of a proton. In this case, however, we have also present the Cl atom, and since Cl has a greater tendency to form a negative ion than NO (HCl is much more ionised than $H_2N_2O_2$) it is split off instead of the NO group. The primary process is thus

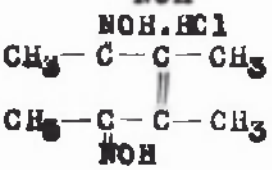


(A)

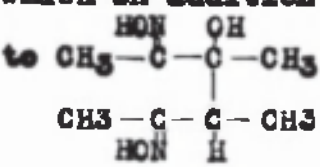
This primary process is then followed by secondary processes. The first is the condensation of 2 molecules of (A).

(B)

(B) then adds on HCl to give

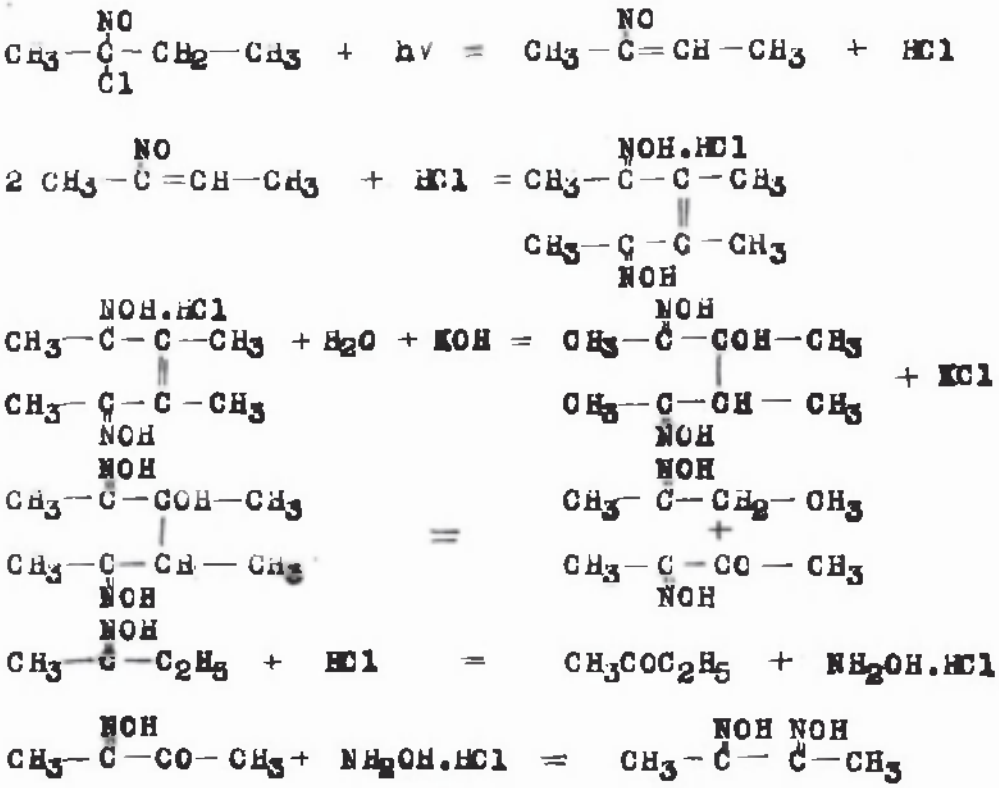


which on addition of water and neutralisation is hydrated to



. The latter compound then splits up

to give methyl ethyl ketoxime and diacetyl monoxime. A little of the methyl ethyl ketoxime is hydrolysed to methyl ethyl ketone and hydroxylamine which then condenses with the diacetyl monoxime to give dimethyl glyoxime. The complete mechanism is thus represented by the following scheme:-



Decomposition of βChloroβnitrosohexane by Red Light in the Absence of Oxygen.

In these experiments 5% solutions of chloronitrosohexane in methyl alcohol were used, and they were decomposed in the same way as the solutions of chloronitrosobutane. The amount of HCl liberated was estimated by

titrating a decomposed solution of known strength with standard alkali or silver nitrate. 4ccs. of a 0·8791% solution of chloronitrocyclohexane after decomposition were equivalent to 11·6ccs. of a 0·09478N $Ba(OH)_2$ solution. That is, the HCl present is equivalent to 93·2% of the total chlorine in the compound.

The alcohol was evaporated under reduced pressure when an oily residue was obtained. The oil was added to water and neutralised, when a brown layer separated on top. This layer was extracted with ether and distilled at a pressure of 6mm. A fraction of a colourless liquid B.Pt. 80°C/6mm. was obtained. A brown oil was left in the flask. It charred if attempts were made to distil it. The aqueous layer was evaporated to dryness and the solid residue extracted with ether. No product was obtained.

The liquid distilling at 80°C/6mm. was thought to be methyl butyl ketoxime B.Pt. 80°C/6mm. It gave n_D^{20} 1·4481. A sample of methyl butyl ketoxime gave n_D^{20} 1·4470. A little of the liquid was steam distilled with HCl, the distillate buffered with sodium acetate and treated with semicarbazide hydrochloride. A white crystalline solid was obtained, which after recrystallisation from alcohol gave M.Pt. 124·5°C. A sample of the semicarbazone from methyl butyl ketone had M.Pt.124·5°C.

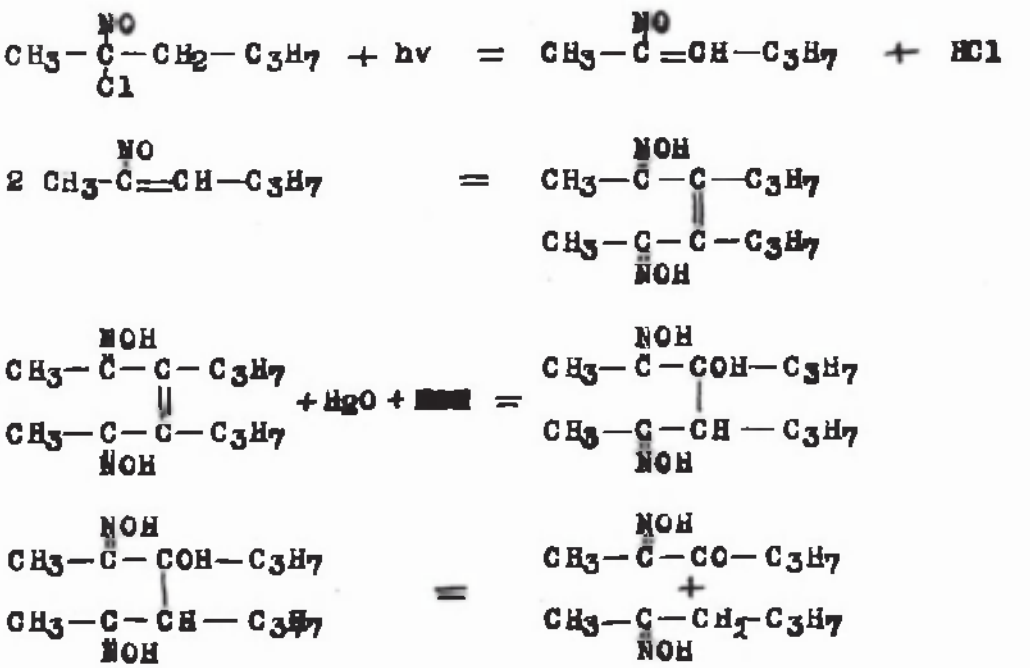
and a mixed melting point showed no depression. From 20gms. of chloronitrosohexane 6gms. of methyl butyl ketoxime were obtained.

Since it has been proved that methyl butyl ketoxime is one of the decomposition products, it was thought that the reaction would be similar to that for chloronitrosobutane. It was therefore decided to see if the compound corresponding to diacetyl monoxime could be detected. It was thought that it would be present in the oily residue after distilling off the methyl butyl ketoxime, and as it could not be distilled it was decided to convert it to the dioxime and prepare the nickel complex.

Some of the oil left in the flask was therefore added to a solution of nickel sulphate and hydroxylamine hydrochloride. The whole was made just alkaline with ammonia and shaken for several days. An orange red precipitate separated. (The nickel complex of the dioxime of 2-3-diketohexane is an orange red solid M.Pt. 144°C.) The red solid was found to consist of a coating of red on a white solid. The red complex was washed with ether when the white solid was left behind. On recrystallisation from the ether solution, the orange red complex had M.Pt. 143°C. This establishes it as the complex from diketohexane dioxime. The white solid, after recrystallisation from aqueous alcohol had M.Pt. 168°C.

This, together with the formation of the nickel complex from it, identifies it as the dioxime of 2-3-diketohexane M.Pt. 168°C. Our original hypothesis has thus been confirmed and the monoxime of diketohexane is evidently a decomposition product. The compound corresponding to $C_8H_{16}N_2O_3$ cannot be isolated as it is probably more unstable. This is borne out by the fact that the yield of methyl butyl ketoxime is greater than the yield of methyl ethyl ketoxime from chloronitrosobutane.

It is thus evident that the reaction mechanism is the same for chloronitrosohexane as for chloronitrosobutane. It is represented by the following scheme.

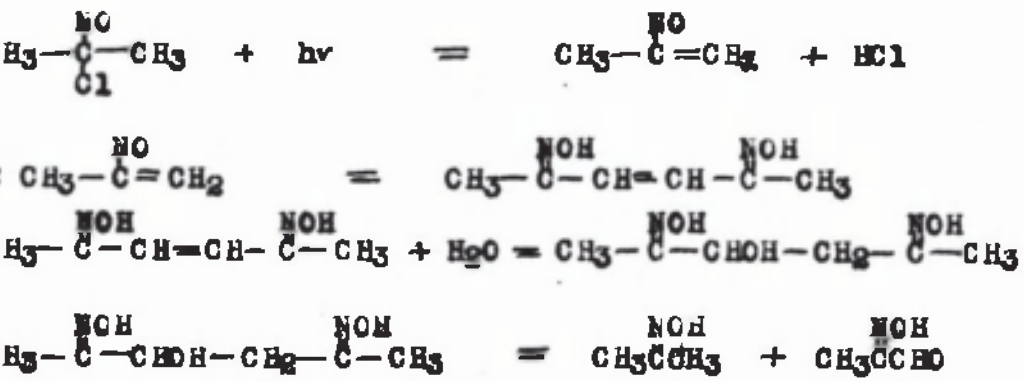


Decomposition of β-Chloronitrosopropane by Red Light in the Absence of Oxygen.

For this compound 5% solutions in methyl alcohol were again used. The method of decomposition was the same as for chloronitrosobutane. The amount of HCl was estimated by titration with standard alkali. 4ccs. of a 4·806% solution of chloronitrosopropane in methyl alcohol required after decomposition 7·1ccs. of 0·2355N alkali. This corresponds to 92·3% of the total chlorine.

The alcohol was evaporated off under reduced pressure and a small amount of a brown oil was left. The oil was dissolved in water and neutralised. On extraction with ether and distillation, a white solid was obtained. M.Pt. 61°C. Mixed melting point with acetoxime 61°C. No other product was obtained. Evaporation of the aqueous layer to dryness and extraction in a Soxhlet with ether gave only a trace of oil. From 10gms. of chloronitroso-propane only 1gm. of acetoxime was obtained. It is thus evident that a large loss has occurred, probably due to the decomposition products evaporating along with the methyl alcohol. In a second experiment therefore, the alcohol was collected by cooling in a freezing mixture as it was evaporated. It was then fractionated at ordinary pressure. It gave a fraction boiling at 64°C and another boiling above 64°C. It was thought that the latter fraction might contain the diketone CH_3COCHO.

It was buffered with sodium acetate and treated with a solution of phenylhydrazine hydrochloride. A yellow precipitate was obtained. As the phenylhydrazone from acetone is a liquid the presence of acetoxime did not interfere. The yellow solid was separated and recrystallised from dilute alcohol. It melted at 145°C. The osazone of CH_3COCHO melts at 145°C. A nitrogen estimation on the compound gave N 22·3% while the value calculated for the osazone of CH_3COCHO is 22·2% N. It has thus been proved that the compound CH_3COCHO is one of the decomposition products. The compounds from which acetoxime and CH_3COCHO are derived could not be isolated, as they are present in the alcoholic HCl solution, and any attempt to isolate them leads to their decomposition. The fact that their decomposition products have been isolated is strong evidence that they are present, however. It is thus concluded that the decomposition of chloronitrosopropane proceeds in a similar manner to that of chloronitrosobutane.



Decomposition of Chloronitroso Compounds by Red Light in the Presence of Oxygen.

In the course of his work on the preparation of chloronitroschexanes by the action of NOCl on normal hexane under the influence of light, Carson (29) noticed that while chloronitroschexane solutions in hexane deposited an oil when exposed to bright sunlight in open tubes, they decomposed without deposition of oil in weak light, and concluded that photo-oxidation had taken place. He also decomposed the compounds in oxygen and measured the amount of oxygen absorbed, but he did not attempt to isolate any oxidation product. It was thus thought desirable to study in more detail the photo-oxidation of these chloronitroso compounds.

The apparatus used in the photo-oxidation experiments is shown in Fig. 1. It is simply a modification of the catalytic hydrogenation apparatus described by Shaefer (30).

A is a flask, the long neck of which is fitted with a tap T_1. It has also a side-arm used for filling it. B is an inverted measuring cylinder containing water and connected to the flask A by the tube C which goes to the top of the cylinder. It is also connected to the water reservoir as shown. The whole is mounted on a board pivoted at the points P and attached to an eccentric

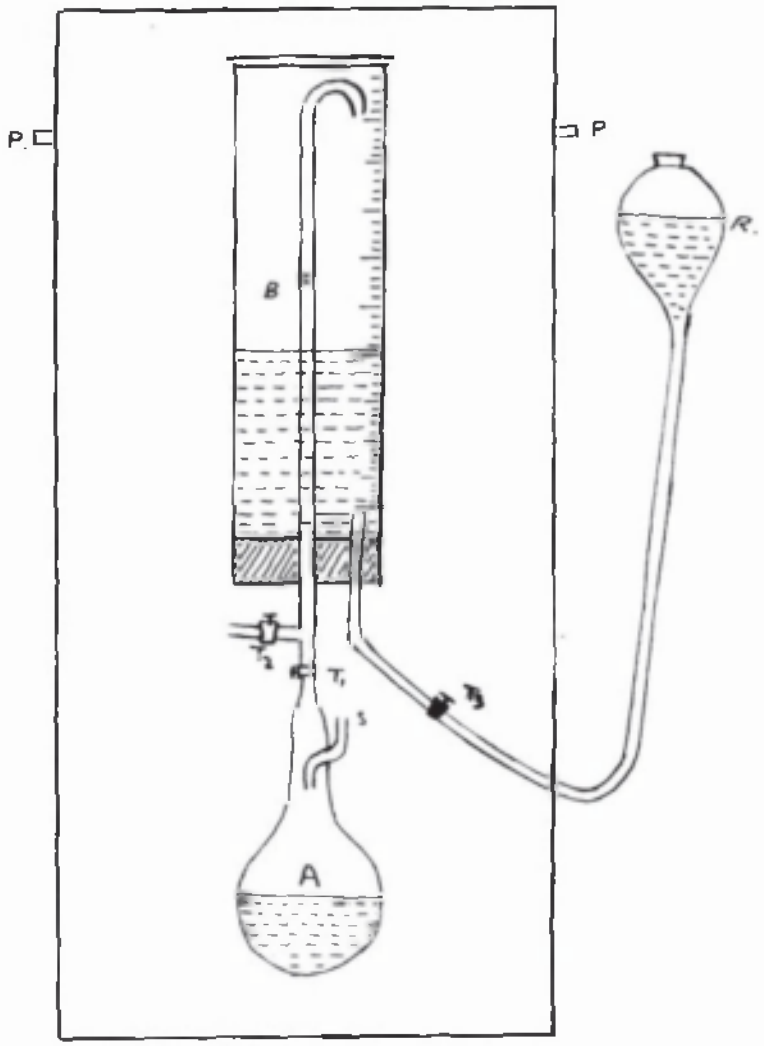


FIGURE 1. Photo-oxidation Apparatus.

wheel at the bottom so that the whole apparatus can be shaken.

A solution of the chloronitroso compound is introduced into the flask A. With tap T_1 open and T_2 and T_3 closed, the tube S is connected to the pump and the whole apparatus evacuated. S is then closed and oxygen passed in at T_2 till the pressure is normal, when T_3 is opened and all the water is driven out of the cylinder. This process is repeated three times when the whole arrangement is filled with oxygen. The side-arm S is then closed and the level of the water in the cylinder adjusted to the zero mark. The motor turning the eccentric is then switched on so that the liquid in the flask is continuously well shaken. It is illuminated by the light from three filament lamps placed close to the flask. No cooling is necessary as the draught caused by the movement of the flask is sufficient to keep it cool. As oxygen is used up in the photo-oxidation, the water in the measuring cylinder rises, and so the volume of oxygen absorbed can be read from the rise in level of the water.

Photo-oxidation of β-Chloro-α-nitrosobutane.

20gms. of chloronitrosobutane were dissolved in methyl alcohol to make 150ccs. of solution. The solution was put in the photo-oxidation apparatus and illuminated. After about 60-70 hours of illumination, the solution had

become completely colourless and 2·7 litres of oxygen had been absorbed. Since chloronitrosobutane decomposes without oxygen, it was expected that the photo-oxidation and the photolysis would proceed simiitaneously, and since the photolysis liberates HCl it was thought that its presence would give an estimation of the amount decomposed without oxygen. The solution was therefore titrated with standard alkali, when it was found that 6ccs. solution required 11ccs. of 0·2355N NaOH for neutralisation. That means that only half of the chloronitrosobutane present had been oxidised.

Hammick and Lister (11) in a work concurrent with this, found that when βchloroβnitroso$\alpha\alpha$dimethylbutane or chloronitrosocyclohexane was photo-oxidised, the corresponding chloronitro compound was obtained. It was therefore decided to see if βchloroβnitrobutane could be isolated from the solution in this case.

The alcohol was evaporated from the solution under reduced pressure and the oily residue added to water. Two layers were formed so that one product is insoluble in water. This product was separated off and the water extracted with ether. The ether extract was added to the oil, dried over anhydrous sodium sulphate and distilled under reduced pressure. A small amount of a colourless liquid B.Pt. 45°C/14mm. was obtained. It had n_D^{20} 1·4369. βChloroβnitrobutane prepared by the oxidation of βchloro-

βnitrosobutane with nitric acid had a B.Pt. 44°C/13mm. and n_D^{20} 1·4371. A chlorine estimation by Stepanow's method gave 25·6% Cl. The value calculated for $C_4H_8O_2NCl$ is 25·7% Cl. The product was thus proved to be αchloroβnitrobutane.

On neutralising the aqueous layer after extracting with ether, and working it up as in the decomposition in the absence of oxygen, methyl ethyl ketoxime, diacetyl monoxime and the compound $C_8H_{16}N_2O_3$ were obtained. This confirms the fact that the oxidation and the photolysis occur simultaneously.

When we consider the volume of oxygen absorbed, namely 2·7 litres of oxygen for 10gms. of chloronitrosobutane, we see that it is much more (almost 3 times) than is required for a simple oxidation from the chloronitroso to the chloronitro compound. Further, the absorption of oxygen does not stop when the illumination stops but proceeds for a time in the dark. Gordon (31) found a similar phenomenon in the case of the photo-oxidation of pseudo nitrols, and attributed it to the further oxidation in the dark of the dinitro compound to the ketone and nitric acid. Tests for oxy-acids of nitrogen were therefore carried out and gave positive reactions. Tests for the presence of ketone were impossible because of the presence of oxime formed in the photolysis in the absence of oxygen. It is thus very probable that a further

oxidation of the chloronitro compound in the dark occurs in this case also, oxy-acids of nitrogen being liberated. This was confirmed by shaking some chloronitrobutane in the apparatus with oxygen. It absorbed oxygen and after 2 days shaking, it gave positive tests for nitrous and nitric acids, and also traces of HCl.

From the above experiments, it would seem that the action of red light on βchloroβnitrosobutane in the presence of oxygen is to bring about the following reaction.

$$CH_3-\underset{Cl}{\overset{NO}{C}}-C_2H_5 + O + \text{Light} = CH_3-\underset{Cl}{\overset{NO_2}{C}}-C_2H_5$$

This is followed by further absorption of oxygen in the dark, with the formation of oxy-acids of nitrogen and other products not isolated.

Photo-oxidation of βChloroβnitrosohexane.

20gms. of chloronitrosohexane were made up to 170ccs. of solution with methyl alcohol and photo-oxidised. 50 hours illumination were required and 2·3 litres of oxygen were absorbed.

10ccs. of the solution were equivalent to 17·5ccs. of 0·2355 N NaOH, so that approximately 60% of the chloronitrosohexane had been photo-oxidised. The oxygen is about twice the theoretical amount required to oxidise chloronitrosohexane to chloronitrohexane. Tests for

oxy-acids of nitrogen gave positive reactions, so it is evident that the oxidation has proceeded further than the chloronitro compound in this case also.

The alcohol was evaporated from the solution under reduced pressure, and the oily residue added to water. The insoluble part was extracted with ether, dried and distilled under reduced pressure. A colourless liquid B.Pt. 70-72°C/14mm. was obtained. Yield 5gms. The liquid gave Cl 21·4%. Calculated for $C_6H_{12}O_2NCl$ 21·5%. The compound is evidently βchloroβnitrohexane.

The aqueous layer on neutralisation, extraction with ether and distillation yielded methyl butyl ketoxime.

Here again the reaction is evidently a simple oxidation, followed by further oxidation in the dark.

$$CH_3-\underset{Cl}{\overset{NO}{C}}-C_4H_9 + O + \text{Light} = CH_3-\underset{Cl}{\overset{NO_2}{C}}-C_4H_9$$

Photo-oxidation of βChloroβnitrosopropane.

20gms. chloronitrosopropane were dissolved in methyl alcohol to give 175ccs. of solution and photo-oxidised until the solution was colourless. (60 hours). 2·2 litres of oxygen were absorbed. 5ccs. of the solution were equivalent to 10ccs. of 0·2355 N NaOH, so that 55% oxidation had taken place. The amount of oxygen is therefore double the theoretical amount. Positive tests for oxy-acids of nitrogen were obtained.

The alcohol was evaporated off from the solution, the residue added to water, extracted with ether, dried and distilled under reduced pressure. A colourless liquid B.Pt. 40°C/20mm. was obtained. It gave Cl 28·8%, the calculated value for $C_3H_6O_2NCl$ being 28·75% Cl. The main oxidation product is therefore βchloroβnitropropane, and the reaction can be written:-

$$CH_3-\overset{\overset{NO}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3 \;+\; O \;+\; \text{Light} \;=\; CH_3-\overset{\overset{NO_2}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3$$

On working up the aqueous layer after neutralisation, some acetoxime formed by the decomposition in the absence of oxygen, was obtained.

THE PHOTO-CHEMISTRY OF SOME CHLORONITROSO COMPOUNDS.

Part 3. The Measurement of the Quantum Yield.

It has been explained in the introduction to this thesis that if the Einstein Law of Photo-chemical Equivalence is obeyed, then one gram molecule of the substance will be decomposed by $\frac{28470}{\lambda \text{ microns.}}$ calories of radiant energy of wave-length λ. Hence the quantum yield γ, or the number of molecules decomposed for every quantum of light absorbed is given by the relation:-

$$\gamma = \frac{\text{gm. mols. decomposed.}}{\text{cals. absorbed.}} \times \frac{28470}{\lambda \text{ microns.}}$$

We thus see that the measurement of the quantum yield implies the measurement of two quantities.

(1) Amount of energy absorbed.

(2) Amount of substance decomposed.

The energy absorbed is measured by means of a thermopile and galvanometer previously calibrated against a light source, the energy of radiation of which is known. The amount of substance decomposed can be measured by either chemical or physical means.

It has been explained in Part 1 of this thesis that the quantum yield is important in deciding a mechanism for a photo-chemical reaction. It is also important in the choice of a suitable substance for an asymmetric decomposition. In the following pages there is described

the measurement of the quantum yield for chloronitroso-butane and chloronitrosohexane.

Absorption Spectra.

The absorption spectra of the compounds were measured in the visible region by means of a Goldberg Spectrodensograph. (21). A 2cm. column of an approximately 1% solution in methyl alcohol was used. The actual concentrations, together with the molecular extinction coefficients ε are shown in Tables 1, 2 and 3. The molecular extinction coefficients ε are shown plotted against wave-length λ in Figures 2, 3 and 4. Measurements of the absorption spectra were also carried out using a 1cm. column. The molecular extinction coefficients were the same, showing that the solutions obey Beer's Law.

We see that all the compounds show the characteristic unsymmetrical band due to the NO group at the red end of the spectrum. It is the light within this band which is responsible for the decomposition of the compounds.

For the measurement of the quantum efficiency it is therefore advisable to obtain a beam of approximately monochromatic light of wave-length corresponding to the head of the band. (6500A in the case of chloronitroso-butane). It is also necessary that the source be sufficiently intense to make the exposure of a reasonably short duration. Such a monochromatic beam was obtained

TABLE 1.

Absorption Spectrum of βChloroβnitrosopropane.

Concentration. 0·9612gm/100ccs.

Length of column. 2cm.

(A.)	7000	6900	6800	6700	6600	6500	6430	6400
	2·80	5·03	6·70	8·60	10·6	11·7	12·6	12·1
(A.)	6300	6200	6100	6000	5800	5600	5400	5200
	10·9	9·51	8·39	7·27	5·03	3·52	1·96	0·73

----------oOo----------

TABLE 2.

Absorption Spectrum of βChloroβnitrosobutane.

Concentration. 1·027gm/100ccs.

Length of column. 2cm.

(A.)	7000	6900	6800	6700	6600	6500	6400	6300
	5·32	6·50	8·87	11·5	14·2	15·1	13·6	11·8
(A.)	6200	6100	6000	5800	5600	5400	5200	5000
	10·1	9·10	7·67	5·32	2·66	0·88	0·29	----

----------oOo----------

TABLE 3.

Absorption Spectrum of βChloroβnitrosohexane.

Concentration. 0·998 gm/100ccs.

Length of column. 2cm.

(A.)	7000	6900	6800	6700	6600	6530	6500	6400
	0·75	2·40	4·30	7·80	11·9	14·2	13·8	12·7
(A.)	6300	6200	6100	6000	5800	5600	5400	5200
	11·2	9·55	8·00	6·60	3·70	1·70	0·37	----

----------oOo----------

FIGURE 2.

Absorption Spectrum of βChloroβnitrosopropane.

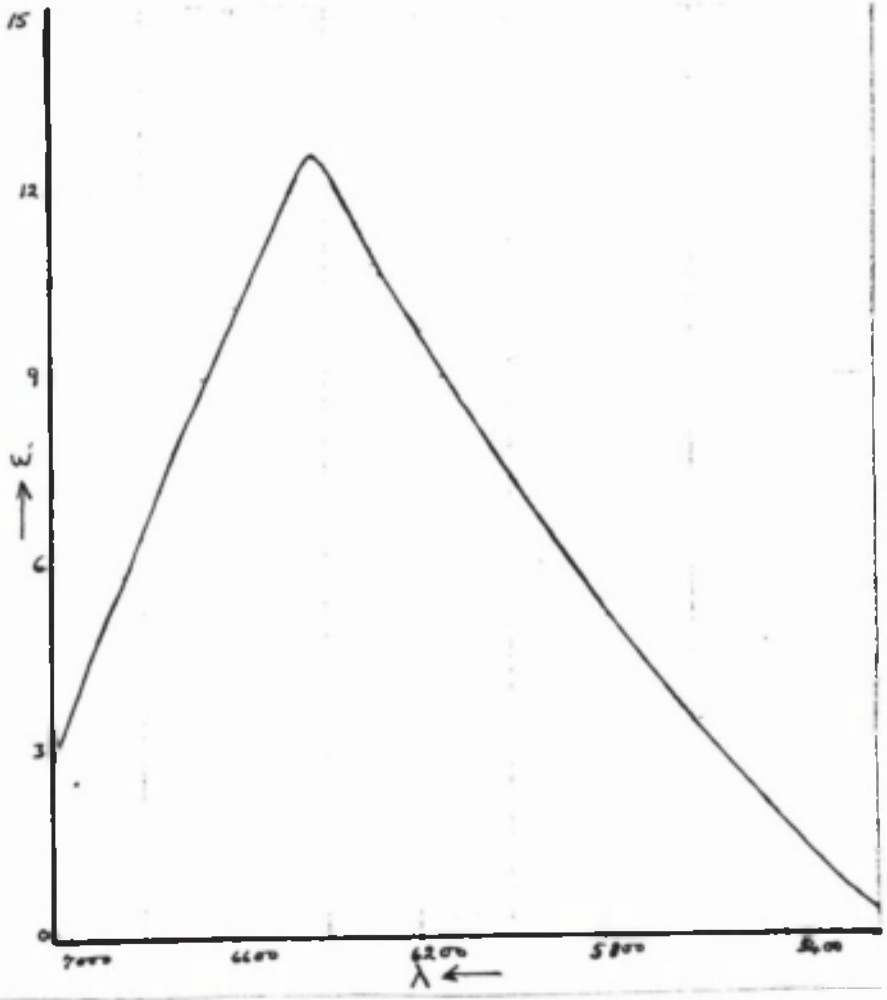


FIGURE 3.

Absorption Spectrum of βChloroβnitrosobutane.

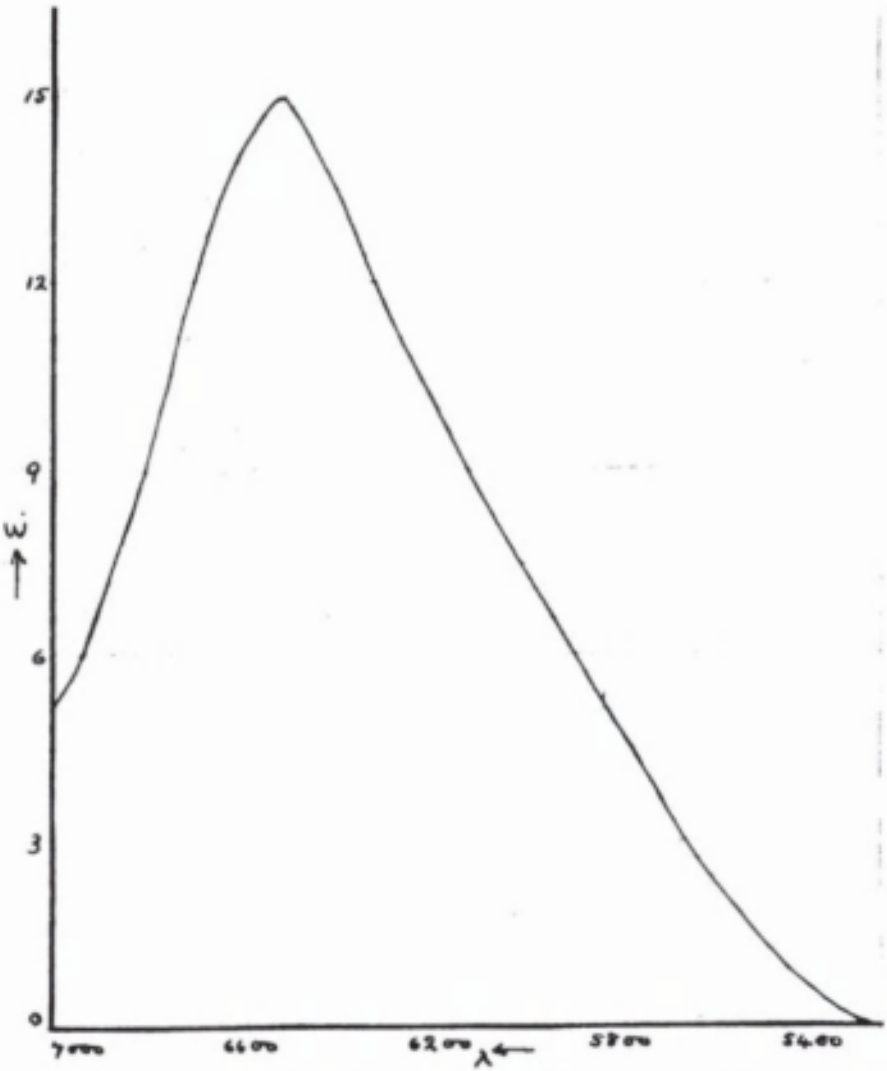
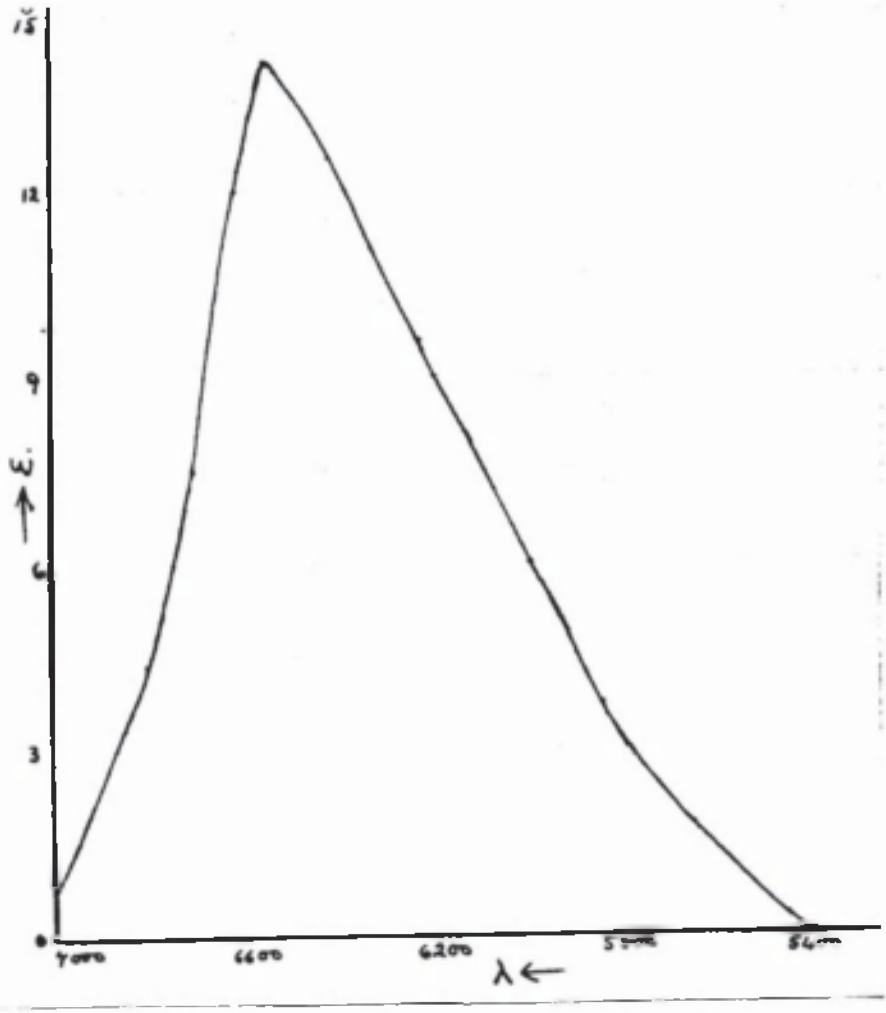


FIGURE 4.

Absorption Spectrum of βChloroβnitrosohexane.



by using the optical arrangement shown in Figure 5.

S is the light source, A and E are lenses of focal length 10cm. and 100cm. respectively, B is a slit 2·6cm. x 1cm., C is a water filter 10cm. thick to cut off infra red radiation, D a red glass filter (Schott and Gen. R.G.2. 2mm. thick), G a thermostat, F a Christiansen filter 7·5cm. thick, H a diaphragm with a sliding shutter, K a screen with a slit 2·6cm. x 1cm., L a glass plate inclined at a small angle, M the cell containing the solution, N a thermopile connected to a sensitive galvanometer and P a Weston Photronic Cell connected to a recording galvanometer.

The light source used was a Zeiss carbon arc with a magnetic feed, supplemented with hand regulation so that the carbons always pulled together to the same position. The arc was run from the D.C. mains, and used a current of 8 amps. We used Conradty cored carbons 6mm. positive and 5mm. negative. It was found that this gave a source of light which was steady to within 10%. All attempts to obtain a steadier arc were unsuccessful. Light from the arc passes through A, B, C, D and E and an enlarged image of the positive crater of the arc is focussed on the thermostat. The face of the thermostat is covered with black paper with a circular hole 6cm. in diameter, just smaller than the Christiansen filter, so that no light could get past the side of the filter.

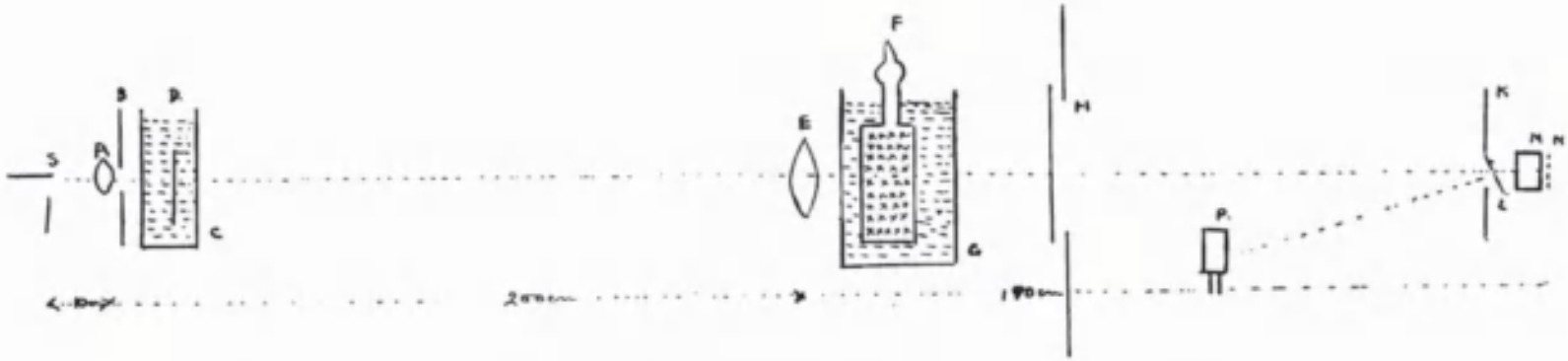


FIGURE 5. Optical Train for Quantum Yield Measurements.

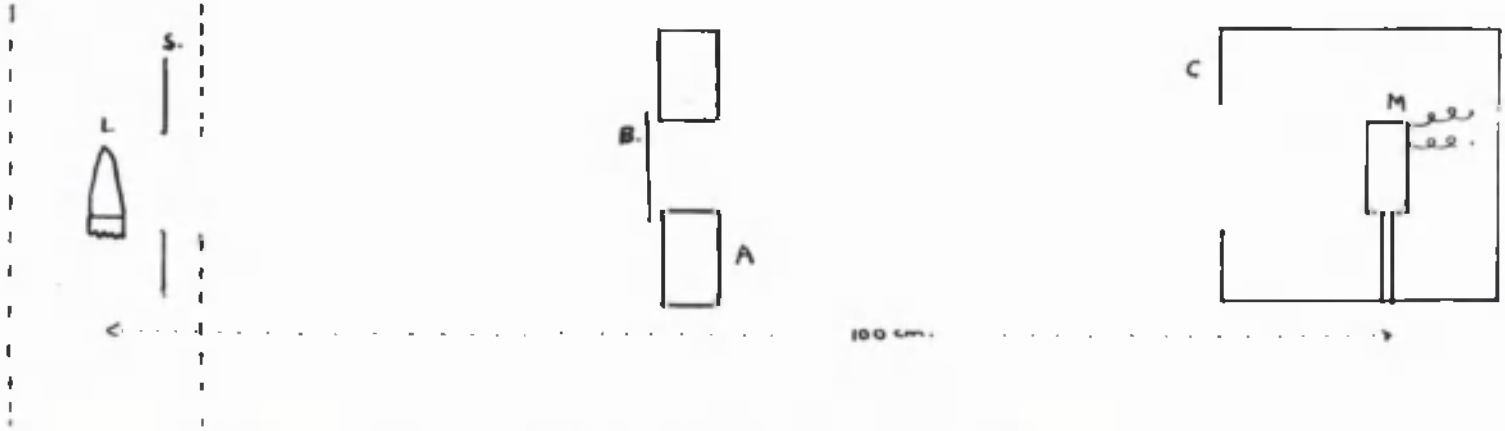


FIGURE 6. Calibration of Thermopile.

The Christiansen filter consists of a suspension of powdered crown glass in methyl benzoate. Light for which the refractive indices of the glass and the methyl benzoate are the same passes straight through it, while light of all other wave-lengths is scattered. Thus, by arranging the temperature of the thermostat, it is possible to obtain a beam of approximately monochromatic light of any desired wave-length. (21).

After passing through the filter, the scattered light is stopped by the screen K, the slit of which is just smaller than the direct beam. A small part of the direct beam is reflected at the inclined glass plate L and falls on the photo-cell P. The photo-cell is connected to a recording galvanometer which thus keeps a record of the variations of the intensity of the light. The recording galvanometer is a mirror galvanometer in which the image of a wire filament is passed through a cylindrical lense and so forms a point of light, which falls on a piece of bromide paper wound on a drum driven by clockwork. On development of the bromide paper, the movement of the spot of light is recorded as a wavy line. An example of such a record is shown in Figure 13.

The remainder of the direct beam passes through the glass plate and an image of the slit B is obtained on the thermopile B. Using the dimensions shown in Figure 4, the size of the image is the same as the size of the slit B.

The thermopile used was a Zeiss model of resistance 50 ohms. It had an exposed surface of 2cm. x 0·4cm. It was used in conjunction with a galvanometer of 50 ohms resistance.

Calibration of the Thermopile.

The thermopile galvanometer system was calibrated against the radiation from a Hefner Lamp. Gerlach (24) measured the energy radiated from such a source and found that the energy falling on an area of 1 square centimetre at a distance of 1 metre from the Hefner Lamp was $2{\cdot}25 \times 10^{-5}$ calories per second.

For the calibration the arrangement shown in Figure 6 was used. The screen S with an aperture 25mm. x 45mm. is placed in front of the lamp L. Beyond the screen is placed a second screen A. This consists of a wooden box 7·8cm. thick, packed with cotton wool. It has also an aperture 60mm. x 30mm. Over the aperture it has a shutter B which can be raised or lowered by a piece of string and a pulley. The shutter is covered with aluminium foil to make it opaque to infra red radiation. C is a wooden box with an opening of 75mm. x 60mm. in it. The thermopile M is enclosed in this box to protect it from draughts. At the suggestion of Professor Fritz Weigert, the Hefner Lamp L was surrounded by a cylinder of wire gauze 18 inches in diameter and about 3 feet high, to protect the

flame from draughts. The arrangement is aligned so that light from any part of the flame can fall directly on any part of the exposed surface of the thermopile. The thermopile is then placed exactly 1 metre from the centre of the flame and its protecting glass removed. The flame of the Hefner Lamp after burning for ten minutes, is adjusted to the correct height. With the shutter S closed, a reading is then taken on the galvanometer. The shutter is then opened and a second reading taken after 30 seconds. (A time greater than the period of oscillation of the galvanometer). Readings are then taken at regular intervals of 30 seconds with the shutter alternately open and closed. The difference between readings with the shutter open or closed is the deflection due to the light. As the zero of the galvanometer shows a drift due to heating of the thermopile, the mean of two consecutive "dark" readings is taken as the zero for the "light" reading which occurs between them. A typical set of readings is shown in Table 4.

Transmission of the Filters.

The wave-length of the head of the band transmitted by the Christiansen filter was obtained by inserting a right angled prism behind L (Fig. 5.) and so reflecting the direct beam into a constant deviation spectroscope. A bright line was then obtained at the wave-length of

TABLE 4.

Calibration of Thermopile Galvanometer System with the Hefner Lamp.

Distance from lamp to thermopile. 100cm.

Distance from galvanometer to scale. 150cm.

Scale Reading. Dark.(cms.)	Scale Reading. Light.(cms.)	Deflection. Difference.(cms.)
21•4		
	15•0	5•45
19•5		
	13•1	5•50
17•7		
	11•4	5•50
16•1		
	10•0	5•50
14•9		
	8•7	5•50
13•5		
	7•5	5•45
12•4		
	6•3	5•55
11•3		
	5•4	5•50
10•5		
	4•4	5•55
9•4		
	3•7	5•50
9•0		
	Average.	5•50

----------oOo----------

maximum transmission of the filter. If the scattered light was examined spectroscopically, it showed a dark line at the wave-length of maximum transmission, due to light of that wave-length not being scattered by the filter.

The effect of the temperature of the thermostat on the wave-length of maximum transmission was found by adjusting the thermostat to a definite temperature for ½ hour, and then examining the light spectroscopically. The wave-length of maximum transmission was found for temperatures at 1 degree intervals between 13° and 19°C. These results are recorded in Table 5 and are shown graphically in Figure 7.

From the graph it is seen that the temperatures required to give light corresponding to the heads of the bands of chloronitrosobutane and chloronitrosohexane (6500A and 6530A) are 15·7°C. and 15·4°C. respectively.

To measure the percentage transmission for different wave-lengths at these temperatures, the method of Elvegarde, Staude and Weigert was used. (21). The method is as follows.

The arc in Fig. 5 was replaced by a 100 watt condensed filament lamp of the same type as the lamp in the spectrodensograph. A lens of 16cm. focal length was placed behind L, and with it and a right angled prism,

TABLE 5.

Effect of Temperature on the Wave-length of Maximum Transmission of the Christiansen Filter.

Temperature, °C.	λmax.(A.)
13°C.	6930A.
14°C.	6770A.
15°C.	6610A.
16°C.	6460A.
17°C.	6300A.
18°C.	6150A.
19°C.	6010A.

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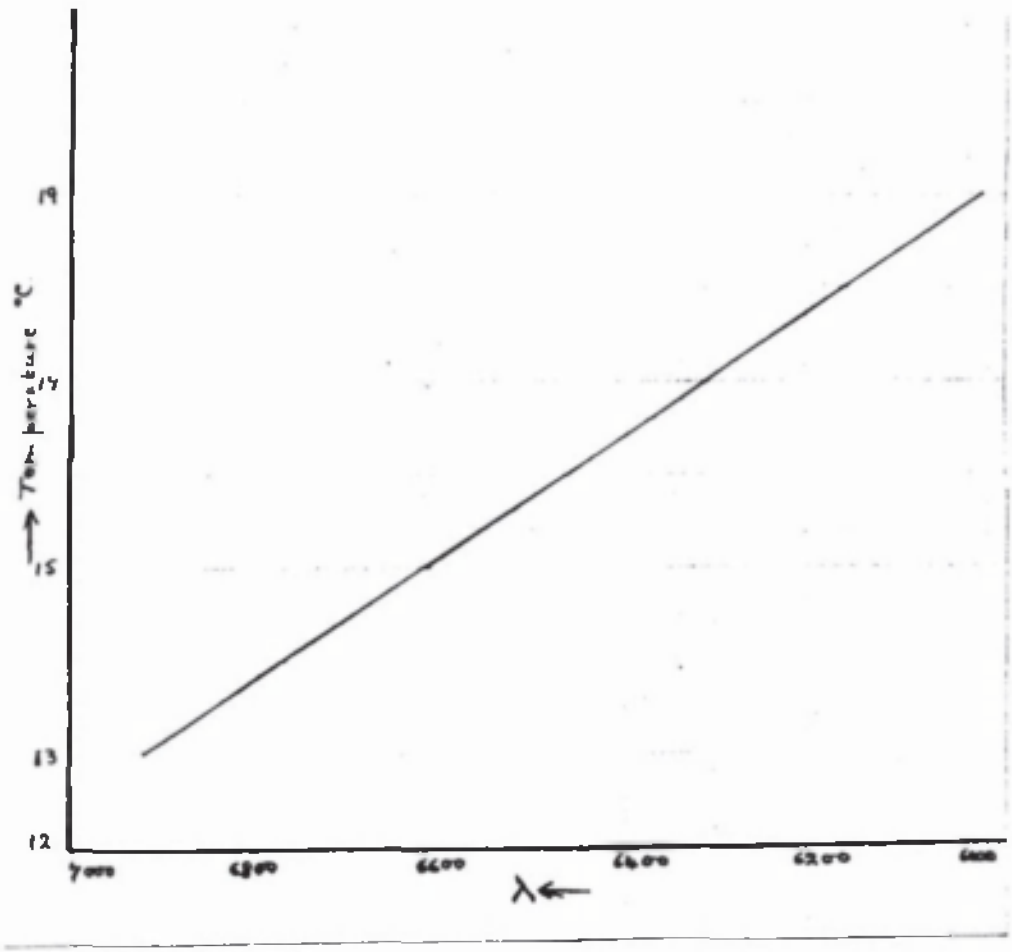
FIGURE 7.

Effect of Temperature on the Wave-length of Maximum Transmission of the Christiansen Filter.



an image of the lamp filament was thrown on the upper part of the slit of the Spectrodensograph. The prism also blocked out the light falling on the upper part of the slit from the Spectrodensograph lamp. The upper field is thus illuminated by light which has been cut down preferentially by the filter, while the lower field is illuminated by the whole of the light from the lamp. The bottom field is then matched with the upper at different wave-lengths by cutting down the lower field by a known amount by means of a uniform grey gelatine wedge. This gives the absorption curve of the filter. From the absorption curve the percentage transmission is calculated. Since the colour density $d = \log \frac{I_0}{I}$, the percentage transmission is equal to the antilogarithm of $2 - d$.

Using this method, the percentage transmission of the following filters was found.

Filter.	Mean Transmission.
(1) Christiansen filter at 15·7°C.	T_1
(2) Schott and Gen. R.G.2. 2mm.	T_2
(3) Christiansen filter at 15·7°C. + Schott and Gen. R.G.2.	T_3
(4) Christiansen filter at 15·4°C.	T_4
(5) Christiansen filter at 15·4°C. + Schott and Gen. R.G.2.	T_5

(1), (2) and (3) are shown in Table 6 and the percentage transmission is plotted against wave-length in Figure 8. The corresponding results for (4) and (5) are shown in Table 7 and Figure 9.

From the curves it is seen that the Christiansen filter gives a beam of light which is fairly monochromatic. It lies well within the absorption band of the compounds, so that complete absorption is easily obtained. The band is made narrower on the short wave side by combining the Christiansen filter with the Schott and Gen. R.G.2. glass filter. This was the combination that was used in the quantum yield experiments. It would seem that this is the first occasion that this filter has been used for photo-chemical work.

In the estimation of the amount of chloronitroso compound decomposed, more difficulty was experienced. At first it was thought that the amount of compound decomposed might be estimated by titrating the amount of HCl set free in the decomposition. This method was found to be impracticable because of the following difficulties.

(1) The amount of HCl set free was not the theoretical amount.

(2) The amount of HCl liberated in a reasonable time of illumination was too small to be accurately determined.

(3) It was not possible to obtain a sharp end-point in

TABLE 6.

Transmission of Filters at 15·7°C.

(A.)	T_1	T_2	T_3
6900	0·4	100	0·4
6800	2·0	100	2·0
6700	7·9	100	7·9
6600	31·6	100	31·6
6550	54·0	100	54·0
6500	71·0	100	71·0
6450	54·0	96·1	52·0
6400	31·6	80·0	20·0
6300	7·9	62·0	5·0
6200	2·0	50·0	1·0
6100	0·4	10·0	---

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FIGURE 8.

Transmission of Filters at 15·7°C.

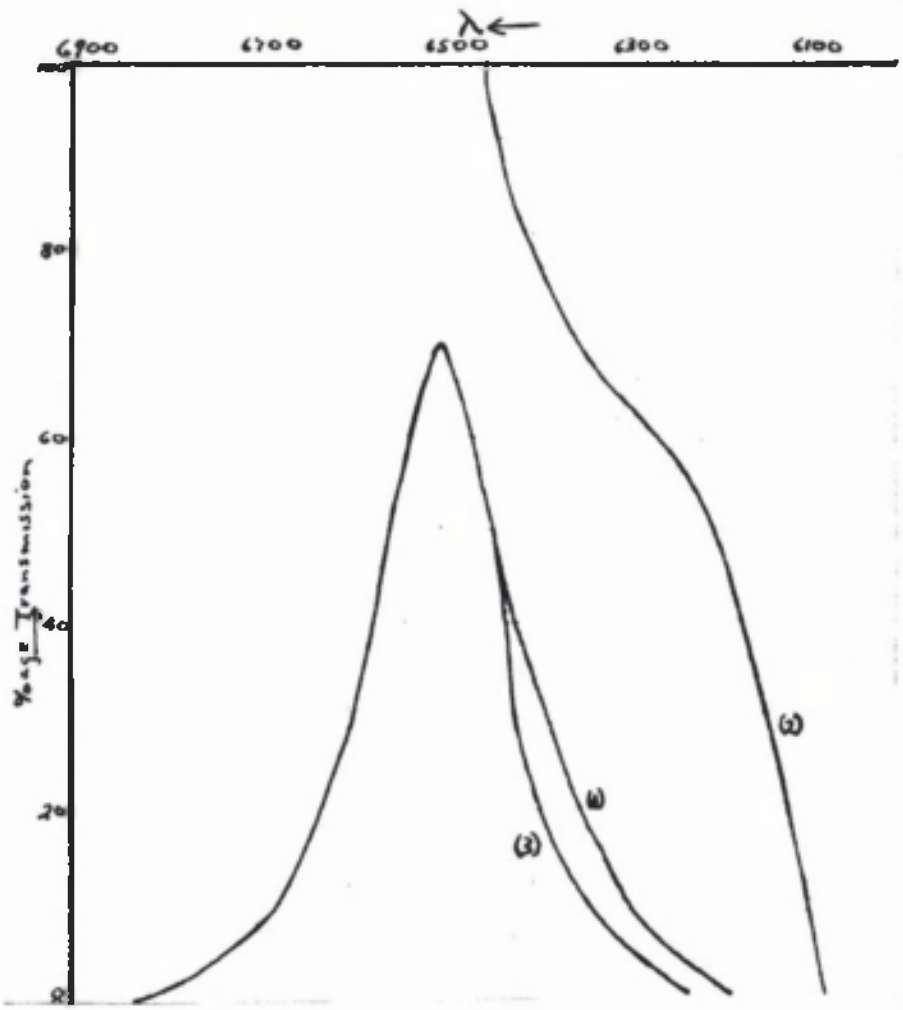


TABLE 7.

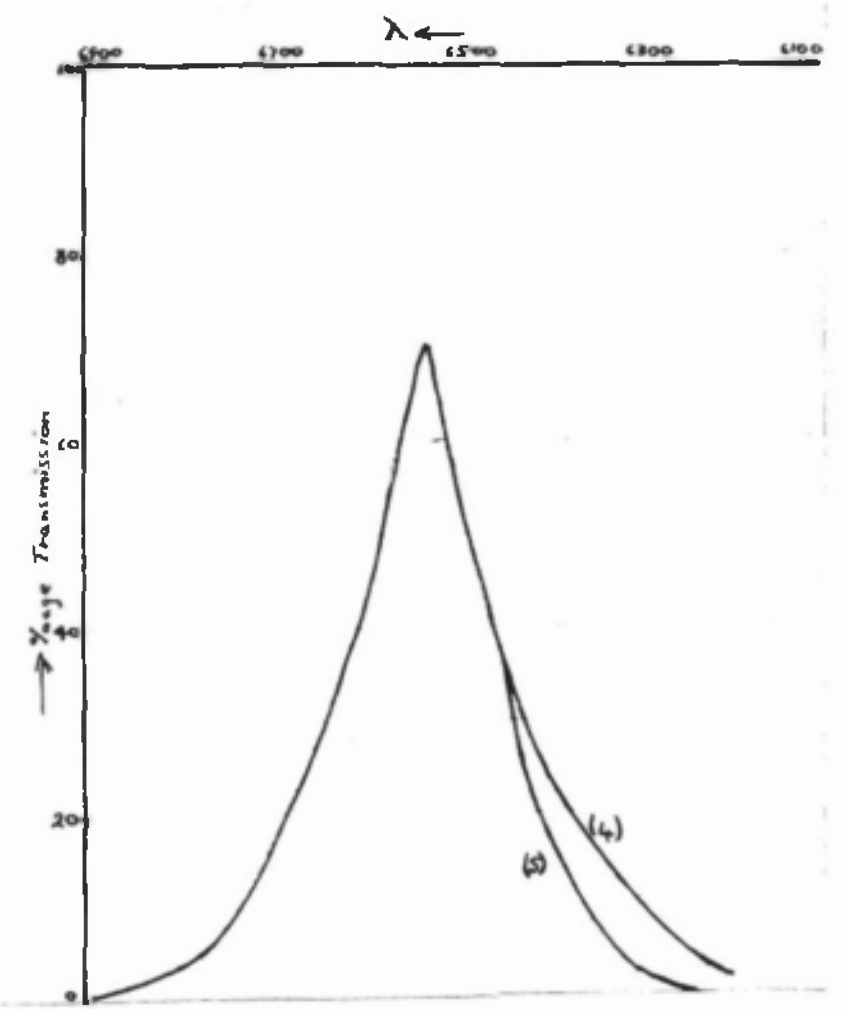
Transmission of Filters at 15·4°C.

(A.)	T_4	T_5
6900	0·8	0·8
6800	4·0	4·0
6700	16·0	16·0
6600	40·0	40·0
6530	71·0	71·0
6500	56·0	56·0
6400	22·0	17·5
6300	10·0	6·1
6200	2·0	1·0
6100	0·3	---

----------oOo----------

FIGURE 9.

Transmission of Filters at 15.4°C.



the titration, owing to the presence of the blue colour of the chloronitroso compound itself.

The chemical method of estimating the amount of decomposition was thus abandoned in favour of a physical method. The method used was the measurement of the decrease of light absorption of the solution. The method was especially convenient as it could be done by the optical train used for the irradiation of the solution.

Two different methods were used. In the first, the light absorption was measured with the carbon arc and the thermopile. In this case a 1% solution of the chloronitroso compound in methyl alcohol was used, and hence the light was not completely absorbed. In the second and more accurate method, a 4% solution was used to give complete absorption. After partial decomposition, the solution was diluted to 5 times the volume and the light absorption was measured by replacing the arc in Fig. 5 by a steady light source, and the thermopile by a Weston Photronic Cell. These two methods are fully described below.

Method 1.

The temperature of the thermostat was adjusted to the required temperature and maintained at it all through the experiment. The experiment was not begun until the temperature of the thermostat had been constant for at

least half an hour. The arc was then switched on and a series of 10-12 readings was taken on the thermopile galvanometer, in the same manner as for the calibration of the thermopile. Simultaneously with these readings, the deflection due to the light falling on the photo-cell was recorded on the recording galvanometer attached to it. These readings give us a relation between the light falling on the thermopile and that on the photo-cell. Thus, henceforth, we can tell the amount of light falling on the space now occupied by the thermopile, if we know the reading on the recording galvanometer attached to the photo-cell.

The decomposition cell (a rectangular glass cell 3 x 0·9 x 1cm. with a ground glass stopper) was filled with alcohol. It was placed in a holder with a slit the exact size of the slit of the thermopile and attached to the front of the thermopile. This facilitated the aligning of the cell and the thermopile. The aligning had to be very carefully done to ensure that all the light which passed through the cell fell on the thermo-pile. A second series of readings was then taken on the thermopile and photo-cell. The cell was dried out and filled with a 1% solution of the chloronitroso compound in methyl alcohol and a third series of readings was taken. The solution was then illuminated for a known period of about three hours, series of six readings each

being taken on thermopile and photo-cell at intervals of 40 minutes. A series of 10 readings was taken at the end of the experiment. During the whole of the period of illumination, the recording galvanometer kept a record of the light falling on the photo-cell.

Calculation of the Change in Concentration.

In every case, each reading on the thermopile was divided by the corresponding reading on the photo-cell and the average of each series was taken. This average gives us the deflection on the thermopile when the deflection on the photo-cell is unity. That is, it gives the deflection on the thermopile under constant illumination. When the cell is filled with alcohol, the ratio is proportional to the incident light I_o. When the cell is filled with solution, the ratio is proportional to the transmitted light I. Hence, since we know the values of I_o and I for all solutions, we can find the concentration from Beer's Law Log $\frac{I_o}{I} = KC$. The fact that the solution obeys Beer's Law over the range of concentration used was verified by taking readings on the thermopile and photo-cell for a number of solutions of known concentration. The results are shown in Tables 8 and 9.

Calculation of the Energy Absorbed.

For each pair of carbons, the average reading on the photo-cell was found from the photographic record by

TABLE 8.

Beer's Law for β-Chloro-α-nitrosobutane.

Conc. gms/100ccs.	I_o	I	K	1/c.logI_o/I.
0·9	3·31	0·2670		1·21
0·72	3·31	0·4333		1·22
0·54	3·31	0·7457		1·20
0·36	3·31	1·248		1·18

TABLE 9.

Beer's Law for β-Chloro-α-nitrosohexane.

Conc. gms/100ccs.	I_o	I	K	1/c.logI_o/I.
1·3	3·836	0·2424		0·9232
1·04	3·836	0·4134		0·9309
0·81	3·836	0·6766		0·9290
0·65	3·836	1·211		0·9103

finding the area between the curve and the zero line. From the ratios $\frac{I_o}{I}$ already found, the percentage absorption was calculated and graphed against time. From the graph the mean percentage absorption was found for each pair of carbons. This was multiplied by the mean deflection on the photo-cell for the particular carbon, and by the ratio of the thermopile deflection to the photo-cell deflection with the decomposition cell removed. In this case, the glass in front of the thermopile compensates for the glass of the decomposition cell and hence gives the true value of the light falling on the solution. The result obtained is the energy absorbed per second in galvanometer deflection units. It is converted to calories/second by multiplying it by the factor $2{\cdot}25 \times 10^{-5} \times 0{\cdot}8/A$, where $2{\cdot}25 \times 10^{-5}$ cals./sq.cm./sec. is the energy from a Hefner Lamp at a distance of 1 metre (24), A is the deflection on the thermopile galvanometer system given by the radiation from a Hefner Lamp at a distance of 1 metre, and 0·8sq.cm. is the area of the exposed surface of the thermopile, and hence also of the solution. The result when multiplied by the time in seconds for which the carbon was illuminating the solution, gives the energy absorbed in that time. The total energy is found by summing the energy for each carbon.

Knowing the amount of substance decomposed and the amount of energy absorbed, the quantum yield is calculated

from the relation

$$\gamma = \frac{\text{Moles decomposed}}{\text{Calories absorbed}} \times \frac{28470}{\lambda \text{ microns}}.$$

Some results using this method are shown in Tables 10 and 11.

The use of the photo-cell as a means of recording the variations in intensity of the light source is a noteworthy feature of this method and also of the second method to be described. To give accurate results it must be known that the deflection on the photo-cell is proportional to the intensity of the light. The constancy of the ratio of thermopile deflection to photo-cell deflection obtained shows that this is the case, at least over the range of intensity met with in the actual experiments. An example of the sort of agreement obtained in the ratio of thermopile readings to photo-cell readings is given in Table 12. It will be seen that the values are constant over the range of intensity which occurs in the experiment. (A 10% variation).

This method of measuring quantum yields suffers from certain disadvantages. In the first place, the light is not completely absorbed. This makes necessary the measurement of the amount of absorption at frequent intervals, and from a graph, finding an average value of the absorption. This makes the calculation very laborious. In addition, the inaccuracy of the result is increased by the fact that the light is not constant, and hence the

TABLE 10.

Quantum Yield for β-Chloro-β-nitrosobutane. (Method 1.)

Initial concentration. 1·0gms/100ccs.

Volume of cell. 2·7ccs.

I_o alcohol in cell. 3·178.

I_o cell removed. 4·123.

Time(mins.)	I	Conc.	Moles decomp.
0	0·2009	1·0	------
20	0·2010	---	------
40	0·2308	---	------
60	0·2332	---	------
100	0·2566	---	------
140	0·3123	---	------
180	0·3544	0·7934	$4·46 \times 10^{-5}$
220	0·3977	0·7518	$5·36 \times 10^{-5}$
260	0·4457	0·7114	$6·22 \times 10^{-5}$

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Carbon.	1	2	3	4	5	6	7
Time of illumination(mins)	43	40	40	40	40	40	20
Av. photocell deflection (mm)	141	138	136	126	137	142	138
Mean %age absorption.	93·1	92·3	91·2	89·9	88·4	86·9	85·7
Energy(cals)	·4514	·4087	·3970	·3638	·3815	·3948	·1900

----------oOo----------

Time (mins)	Energy (cals)	Moles decomposed.	Quantum Yield.
180	1·82	$4·46 \times 10^{-5}$	1·07
220	2·20	$5·36 \times 10^{-5}$	1·07
260	2·587	$6·22 \times 10^{-5}$	1·06

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TABLE 11.

Quantum Yield for βChloroβnitrosohexane. (Method 1).

Initial concentration. 0·996gms/100ccs.

Volume of cell. 2·9ccs.

I_o alcohol in cell. 3·411.

I_o cell removed. 4·383.

Time(mins)	I	Conc.	Moles decomp.
0	0·4043	0·996	------
40	0·4801	-----	------
80	0·5724	-----	------
120	0·6684	-----	------
160	0·7455	0·7131	$5·55 \times 10^{-5}$
200	0·8585	0·6469	$6·822 \times 10^{-5}$
240	0·9302	0·6092	$7·559 \times 10^{-5}$

----------oOo----------

Carbon.	1	2	3	4	5	6	7
Time of illumination(mins)	20	40	40	40	40	40	20
Av. photocell deflection(mm)	151	150	153	151	151	147	146
Mean %age absorption	88·1	86·9	83·2	80·3	78·1	74·8	72·7
Energy(cals)	·2254	·4374	·4331	·4124	·4029	·3760	·1831

----------oOo----------

Time (mins)	Energy (cals)	Moles decomposed.	Quantum Yield.
240	2·47	$7·55 \times 10^{-5}$	1·32
200	2·10	$6·82 \times 10^{-5}$	1·40
160	1·71	$5·59 \times 10^{-5}$	1·40

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TABLE 12.

Relation between Thermopile Deflection and Photo-cell Deflection.

Thermopile deflection.(mm)	Photo-cell deflection.(mm)	Ratio.
475	120	3·959
476	118	4·053
475	117	4·060
460	116	3·966
451	115	3·922
456	114	4·000
450	113	3·982
444	111	4·000
441	111	3·973
470	117	4·017
458	117	3·917
475	118	4·025
480	119	4·033

average calculated is not correct, as each value is not assigned the correct weight factor, but all are given the same weight. Secondly, the change in concentration cannot be measured with sufficient accuracy, because of the variations in the intensity of the light source. It was therefore decided to alter the method to eliminate these errors. The first error was eliminated by using a 4% solution of the chloronitroso compound, and so obtaining complete absorption of the light. It was diluted at the end of the experiment to allow the change in the concentration to be measured. This dilution is necessary, because at the higher concentration, the change in the amount of light transmitted, with the change in concentration, is too small to be accurately determined. At the lower concentration, the change in transmission with concentration is much more pronounced. In order to increase the accuracy of the concentration measurements, the arc was replaced by a constant light source. As all sources which are likely to be constant are much weaker than the arc, it was necessary to obtain a method of measuring the light transmission which would be more sensitive than the thermopile. This was obtained in the Weston Photronic Cell. It also had the advantage that its zero did not alter in the same way as that of the thermopile.

The arc and the thermopile were thus retained for

the irradiation and the measurement of the energy, but they were replaced by a constant light source and the photo-cell for the measurement of the concentration of the solution at the end of the experiment.

Considerable difficulty was met with in the finding of a suitable lamp for the absorption measurements. Such a lamp must be steady, and yet give a beam of sufficient intensity to give a deflection of the order of 50cm. on the photo-cell. Several lamps were tried. The steadiness was found by attaching the photo-cell to the recording galvanometer and then taking a record of the intensity over a period of half an hour. These records are shown in Figures 10, 11, 12 and 13 for the following lamps.

(1) 100 watt filament lamp run off the mains. Fig. 10.

(2) 100 c.p. Pointolite lamp run off the mains. Fig. 11.

(3) 100 watt condensed filament projection lamp run off 12 volt batteries. Fig. 12.

(4) Carbon arc run off the mains. Fig. 13.

In the case of the carbon arc, the intensity had to be cut down by an iris diaphragm to keep the record on the paper. The arc is a very intense source, but it is steady to only 10%. The two mains lamps are also unsteady. This points to fluctuations in the mains voltage. The Pointolite is less variable than the filament lamp, probably due to the inertia of the larger mass of metal in it.

FIGURE 10. Filament Lamp off Mains. Deflection 30cm.

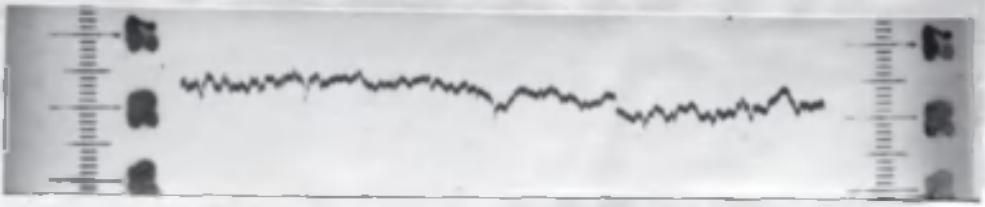

FIGURE 11. Pointolite Lamp off Mains. Deflection 30cm.

FIGURE 12. Projection Lamp off Cells. Deflection 30cm.

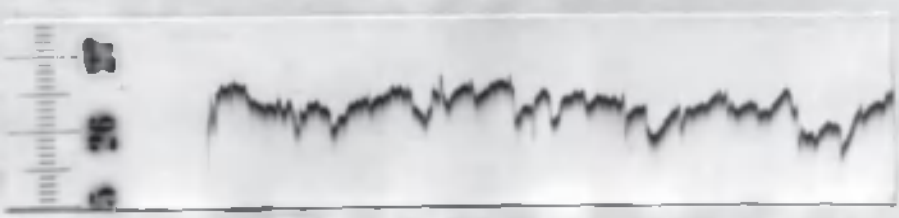

FIGURE 13. Carbon Arc off Mains. Deflection 10cm.

The condensed filament projection lamp run off 12 volt storage batteries gives a light source which is steady to 1 part in 500. As it gives in addition, a deflection of 70cm. on the galvanometer scale it is ideal for the measurement of the concentration.

The final technique developed fro the measurement of the quantum yield is described below.

Method 2.

The thermostat was adjusted to the correct temperature and maintained at it all through the experiment. After the temperature had been constant for half an hour, the arc was switched on and a series of readings was taken on the thermopile, and simultaneously, the light falling on the photo-cell was recorded on the drum camera. The thermopile was then taken away and the decomposition cell (an airtight glass cell 3·0 x 0·9 x 1·0cm. with a ground glass stopper) filled with a 4% solution of the chloronitroso compound in methyl alcohol was placed so that the slit in front of it occupied the exact position formerly occupied by the slit of the thermopile. This was done by having the cell-holder attached to the front of the thermopile, which was then moved back a distance equal to the thickness of the cell-holder. Since the two slits were identical in size, it follows that the thermopile and the solution would receive the same amount of

light, if the intensity of the beam were constant. Therefore the ratio between the thermopile reading and the photo-cell reading will enable us to calculate the light falling on the solution, if we know the reading on the photo-cell. In that position, the solution was irradiated for a period of 7½ hours, a record of the light falling on the photo-cell being kept all the time. The cell was then removed, 2ccs. of the partly decomposed solution were taken and diluted to 10ccs. with methyl alcohol. The arc was replaced by the projection lamp and the thermopile by the photo-cell. The lamp was switched on and left for a quarter of an hour to become steady. The diluted solution was placed in an open rectangular glass cell 1cm. thick and placed in front of the photo-cell. The scale reading was noted. Similar readings were taken with the cell filled with solutions of known concentration.

In some cases the solutions were made up by weight instead of by volume, to see if greater accuracy could be obtained, but there was no difference in the final result.

Calculation.

From the series of readings taken on the thermopile and photo-cell, the ratio of thermopile readings to photo-cell readings was found and the average value taken. Let

the average ratio be a_1. For each pair of carbons used to irradiate the solution, the average deflection on the photo-cell was found by tracing the record on to squared paper, and finding the area under the curve. The average of all the carbons was then found. Let it be a_2.

Then if $\underline{t}$ be the time of illumination of the solution in seconds, the total energy absorbed is

$$\frac{a_1 \times a_2 \times t \times 0{\cdot}8 \times 2{\cdot}25 \times 10^{-5}}{A} \text{ cals.}$$

where the other figures have the same significance as in page 77.

But as the light falling on the thermopile suffers two reflections at air-glass surfaces, while the light falling on the solution suffers only one reflection at such a surface, since it is absorbed, and hence, does not emerge from the decomposition cell, we must apply a correction of 5% for reflection losses. The total energy falling on the solution is thus

$$\frac{1{\cdot}05 \times a_1 \times a_2 \times t \times 0{\cdot}8 \times 2{\cdot}25 \times 10^{-5}}{A} \text{ cals.}$$

To find the decrease in concentration of the solution, a graph is drawn in which the deflection on the photo-cell with the projection lamp is plotted against concentration. From this graph the concentration of the partly decomposed solution is read. If c_1 gms./100ccs.

is the initial concentration, c_2 gms./100ccs. is the final concentration, V ccs. is the volume of the decomposition cell, and hence the volume of solution used and M is the molecular weight of the compound, then the number of gm. molecules decomposed is

$$\frac{(c_1 - c_2) \times V}{100M}$$

The quantum yield is then given by the relation

$$\gamma = \frac{\text{moles decomposed}}{\text{cals. absorbed}} \times \frac{28470}{\lambda \text{ microns}}$$

The first measurements of the quantum yield of chloro nitrosobutane by this method gave the values 1·37 and 1·39. (Tables 13 and 14). When we attempt to interpret these results, we see that there are two possibilities. The first is that the quantum yield is 2, the low value being due to the deactivation of some of the activated molecules by collisions. The second possibility is that the quantum yield is 1, and the high value is due to one or more of the following factors.

A dark reaction.

The effect of small amounts of oxygen.

A reaction with the HCl set free in the reaction.

The effect of solvent.

Since the reaction product $C_8H_{15}N_2O_2Cl$ contains twice as many carbon atoms as the original chloronitroso

TABLE 13.

Quantum Yield for βChloroβnitrosobutane. (Method 2).

Ordinary methyl alcohol not freed from oxygen.

Conc. gms/100ccs.	0·840	0·756	0·672	0·588	Expt.
Photocell defl. with Proj. Lamp(mm).	144	172	212	156	196

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From graph expt. conc. 0·7956gm/100ccs.

3·528gm/100ccs. before diln.

Initial concentration. 4·21gm/100ccs.

Volume of solution used. 2·85ccs.

Gm. molecules decomposed. $1·549 \times 10^{-4}$

-------oOo-------

Carbon.	1	2	3	4	5	6	7	8	9	10	Av.
Av. Photocell deflection(mm).	120	124	130	128	123	118	122	121	119	125	123

-------oOo-------

Ratio Thermopile defl./Photo-cell defl. 4·969

Deflection on thermopile with Hefner Lamp. 52·5mm.

Energy absorbed. 4·864 cals.

Quantum Yield. 1·39

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TABLE 14.

Quantum Yield for β-Chloro-α-nitrosobutane. (Method 2).

Ordinary methyl alcohol not freed from oxygen.

Conc. gms/100gms.	1·03	0·8682	0·7478	0·6882	Expt.
Photocell defl. with Proj. Lamp(mm).	152	201	246	270	210

From graph expt. conc. 4·219gms/100gms. before diln.

Initial concentration. 5·100gms/100gms.

Weight of solution used. 2·258gms.

Gm. molecules decomposed. $1·638 \times 10^{-4}$

Carbon.	1	2	3	4	5	6	7	8	9	10	Av.
Av. Photocell deflection(mm).	120	138	134	130	133	129	131	134	134	129	132

Ratio Thermopile defl./Photo-cell defl. 4·268

Deflection on thermopile with Hefner Lamp. 55·0mm.

Energy absorbed. 5·828 cals.

Quantum Yield. 1·37

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compound, it seemed at first that the quantum yield would be 2, and that the reaction was one between an activated molecule and an unactivated molecule. If this is true there must be deactivation with the solvent molecules taking place, and so the quantum yield should vary with the concentration, approaching 2 at high concentrations, and being lower at low concentrations.

It was therefore decided to test for the effect on the quantum yield of the following factors.

(1) Dark reaction.

(2) Concentration.

(3) Oxygen.

(4) HCl.

(5) Solvent.

To test for a dark reaction, the following experiment was carried out. A 4% solution of chloronitrosobutane in methyl alcohol was made up. A little of it was diluted to 5 times the volume and the transmission measured with the photo-electric colorimeter already described. A solution of copper sulphate was also made up of a such a concentration that its transmission was the same as the diluted chloronitrosobutane solution. The two solutions were then allowed to stand for 15 hours in the dark. The chloronitrosobutane was diluted 5 times and its transmission measured. The transmission of the copper sulphate was also measured again. The two solutions

were found to give still the same deflection, so that the concentration of the chloronitrosobutane solution had not changed. It is thus proved that there is no appreciable dark reaction.

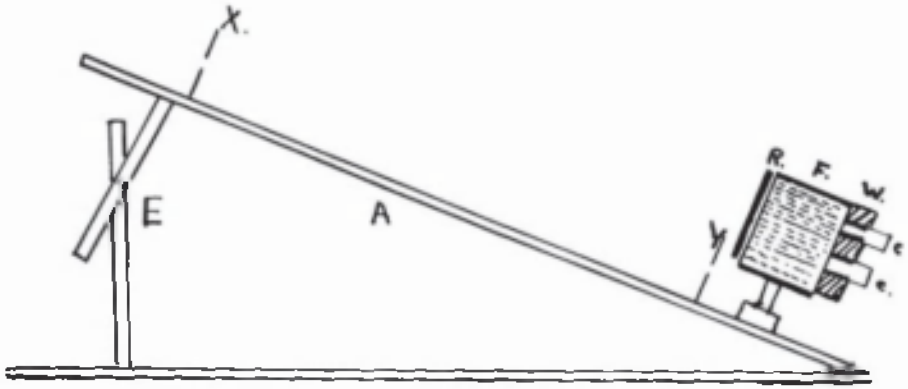
Effect of Concentration on the Quantum Yield.

To find the effect of the concentration on the quantum yield it was decided to carry out some experiments with solutions of different concentrations, exposing them simultaneously to a uniform light and then measuring the amount of decomposition.

For these experiments, the apparatus shown in Figure 14 was used. It consists simply of a piece of wood A, to which a water filter F is rigidly attached. In front of the water filter is mounted a red glass filter R. Behind the water filter is fitted a piece of wood W, in which four holes are bored, close together and on the circumference of a circle. Into these holes brass tubes are fitted, and into the brass tubes go the cells C containing the solution to be decomposed. The brass tubes were cut so that the ends of the cells were always the same distance (about 1") from the end of the brass tube at which the light entered. This was to prevent stray light from entering the cells. The brass tubes were also fitted with diaphragms so that the same area of all the cells was exposed to the light. The

FIGURE 14.

Apparatus for Showing Effect of Concentration, etc. on Quantum Yield.



decomposition cells were made from glass tube of $\frac{3}{4}$" inside diameter. The tubing was ground down to the required length and flat ends cemented on. They were fitted with side-arms for convenience in filling. The side-arms were closed by fitting a piece of glass rod into them and then fitting a rubber sleeve over it. The small space between the solution and the glass rod was filled with nitrogen to prevent photo-oxidation. Two sets of cells were used, 1cm. and 2cm. in length respectively, and they were graduated so that the larger contained exactly twice as much as the smaller. The cells were placed in the holes in the wood with large and small cells alternating, so that if there is any lack of uniformity in the illumination, the solutions in similar cells will not be equally decomposed. They were then mounted behind the water filter and exposed to direct sunlight for about 3 hours. They were kept at right angles to the sun's rays by means of the sighting arrangement X and Y, and the adjustment E for altering the inclination of the board. The sighting arrangement consisted of two pieces of metal. The first piece had a pin-hole which threw an image of the sun on to the second. The sun's image had then to be kept fixed on a definite point on the second metal plate.

Two sets of experiments were carried out, one with 2% solutions in the large tubes and 4% solutions in the

the small tubes, and another with 4% solutions in the large tubes and 8% solutions in the small tubes. Since the concentration multiplied by the thickness of the cell is the same for all the cells, the amount of absorption will be the same in all cases, even if it is not complete. In making up the solutions, nitrogen was bubbled through the alcohol to free it from dissolved oxygen. The space above the solution was also filled with nitrogen. The solutions were placed in position and exposed to direct sunlight for about 3 hours. Stray light was excluded from the back of the solutions by means of a black cloth. After exposure the solutions were removed and diluted; the 8% solution 10 times, the 4% solution 5 times and the 2% solution 2½ times. The diluted solutions were placed in a 1cm. thick open cell and the transmission measured by the arrangement used in the quantum yield experiments. The results are shown in Tables 15 and 16. Col. 1 is the concentration of the original solution, col. 2 is the galvanometer reading with the shutter closed, col. 3 is the corresponding reading with the shutter open, while col. 4, the difference between cols. 2 and 3 is a measure of the transmission, and hence of the concentration.

From the results, it is at once apparent that the quantum efficiency does not change with concentration. It is thus unlikely that the quantum yield is 2. It is probably 1, the high experimental value being due to HCl,

TABLE 15.

Effect of Concentration on Quantum Yield of

βChloroβnitrosobutane.

Conc. of orig. soln.	Dark.	Light.	Difference.
8%.	269	103	166
8%.	269	103	166
4%.	269	103	166
4%.	269	102	167
Unexposed solution.	269	172	97

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TABLE 16.

Effect of Concentration on Quantum Yield of

βChloroβnitrosobutane.

Conc. of orig. soln.	Dark.	Light.	Difference.
4%.	314	106	208
4%.	314	105	209
2%.	314	105	209
2%.	314	105	209
Unexposed solution.	314	210	104

----------oOo----------

oxygen or solvent effect.

Effect of HCl on Quantum Yield.

To investigate the effect of HCl on the quantum yield, the same arrangement as the above was used. The only difference was that all the cells were the same size, namely 2cm. long. One pair of cells was filled with a 4% solution of chloronitrosobutane in methyl alcohol, while the other pair was filled with a solution of exactly the same strength, but which also contained 10% HCl. They were exposed to sunlight in the apparatus for 3 hours, diluted and their transmission measured. As is readily seen from the results in Table 17, the presence of HCl does not affect the quantum yield.

Effect of Oxygen on the Quantum Yield.

A similar method was used to find the effect of oxygen on the quantum yield. In this case, however, the cells used were much bigger and were only half filled with the solution. The other half was filled with oxygen in the one case and nitrogen in the other. They were exposed to uniform illumination, the same area of each being irradiated. The cells were shaken periodically to facilitate the diffusion of the oxygen into the solution. The change in concentration of each was measured as before, and the results are shown in Table 18. It is seen that the compound decomposes about 1½ times as fast in oxygen

TABLE 17.

Effect of HCl on Quantum Yield of β-Chloro-β-nitrosobutane.

Solution.	Dark.	Light.	Difference.
10% HCl.	280	105	175
10% HCl.	280	104	176
No HCl.	280	104	176
No HCl.	280	105	175
Unexposed sol. 10% HCl.	280	180	100
Unexposed sol. No HCl.	280	179	101

TABLE 18.

Effect of Oxygen on Quantum Yield of β-Chloro-β-nitrosobutane.

Gas over Solution.	Dark.	Light.	Difference.
Nitrogen.	289	-39	328
Oxygen.	289	-147	436
Unexposed solution.	289	162	127

---

as in nitrogen.

Elimination of Oxygen in Quantum Yield Measurements.

Since the reaction is more rapid in oxygen, and since no special precautions were taken to exclude oxygen from the solution used in the measurement of the quantum yield, it was decided to repeat the quantum yield measurements, taking such precautions. To eliminate oxygen from the methyl alcohol, it was distilled in an atmosphere of nitrogen and stored over nitrogen until required. To prevent air from leaking into the cell during decomposition, the stopper was made as tight as possible. In one case the decomposition was carried out in a sealed glass tube obtained by grinding a flat face on a piece of glass tubing and sealing the tube after it was filled. Measurements of the quantum yield were carried out with solutions of 4%, 6% and 8% chloronitrosobutane in methyl alcohol. The results are shown in Tables 19, 20 and 21. The values of the quantum yield obtained, 1·23, 1·21 and 1·24 are in quite good agreement with a quantum yield of 1. The slightly high experimental value may be due to traces of oxygen still present or to the effect of solvent.

Effect of Solvent on the Quantum Yield.

The effect of the solvent was investigated by the same apparatus as was used to show the effect of HCl and concentration. Two sets of experiments were carried out.

TABLE 19.

Quantum Yield of βChloroβnitrosobutane. (Method 2).

Alcohol freed from Oxygen. Concentration 4%.

Conc. gms/100ccs.	0·8002	0·7202	0·6402	0·5601	Expt.
Photocell defl. with Proj.Lamp(mm).	169	207	254	311	236

From graph expt. conc. 0·6702gms/100ccs.

3·351gms/100ccs. before dilution.

Initial concentration. 4·001gms/100ccs.

Volume of solution used. 2·7ccs.

Gm. molecules decomposed. $1·444 \times 10^{-4}$

Carbon.	1	2	3	4	5	6	7	Av.
Av.Photocell deflection(mm).	92	89	94	97	96	90	93	93

Ratio Thermopile defl./Photo-cell defl. 6·366

Deflection on thermopile with Hefner Lamp. 55·0mm.

Energy absorbed. 5·128 cals.

Quantum Yield. 1·23

TABLE 20.

Quantum Yield of βChloroβnitrosobutane. (Method 2).

Alcohol freed from Oxygen. Concentration 6%.

Conc. gms/100ccs.	0·7826	0·7224	0·6622	0·6020	Expt.
Photocell defl. with Proj.Lamp(mm).	112	131	152	178	145

From graph expt. conc. 0·6921gms/100ccs.

5·247gms/100ccs. before dilution.

Initial concentration. 6·020gms/100ccs.

Volume of solution used. 2·0ccs.

Gm. molecules decomposed. $1·273 \times 10^{-4}$

Carbon.	1	2	3	4	5	6	7	8	9	10	Av.
Av.Photocell deflection(mm).	155	158	150	148	149	150	152	157	139	141	150

Ratio Thermopile defl./Photo-cell defl. 3·334

Deflection on thermopile with Hefner Lamp. 55·0mm.

Energy absorbed. 4·662 cals.

Quantum Yield. 1·21

TABLE 21.

Quantum Yield of βChloroβnitrosobutane. (Method 2).

Alcohol freed from Oxygen. Concentration 8%.

Conc. gms/100ccs.	0·8040	0·7035	0·6030	0·5025	Expt.
Photocell defl. with Proj.Lamp(mm).	176	216	266	332	220

From graph expt. conc. 6·934gms/100ccs.

Initial concentration. 8·040gms/100ccs.

Gm. molecules decomposed. $1·227 \times 10^{-4}$

Carbon.	1	2	3	4	5	6	7	8	9	10	Av.
Av.Photocell deflection(mm).	112	110	110	110	109	109	110	111	109	113	111

Ratio Thermopile defl./Photo-cell defl. 4·238

Deflection on thermopile with Hefner Lamp. 55·0mm.

Energy absorbed. 4·326 cals.

Quantum Yield. 1·24

In one case, solutions of equal strength in acetone and methyl alcohol were used. In the other, dioxan and methyl alcohol were the solvents compared. Dioxan and acetone were used because the solution remains homogeneous in these solvents. Owing to the fact that solutions of the same concentration in different solvents show slightly different transmissions, a calibration of the transmission of each solution was effected by making up solutions of equal concentration in the different solvents, the concentraiion being approximately equal to the concentration of the solution after decomposition. In this way we were able to account for the difference in transmission due solely to the solvent, and not due to the difference in the rate of photolysis. When this factor was excluded, it was found that the reaction went at different rates in different solvents. The decomposition was most rapid in methyl alcohol, being about 20% slower in acetone and 30% slower in dioxan. The results are given in Tables 22 and 23.

It is thus apparent that the photo-chemical decomposition of βchloroβnitrosobutane by light of wave-length 6500A in the absence of oxygen has a quantum yield of 1. This value is raised to 1·2 in the case of methyl alcohol by the effect of solvent. The quantum yield is independent of concentration between 2% and 8%. It is increased by the presence of oxygen, but is unaffected by HCl.

TABLE 22.

Effect of Solvent on Quantum Yield of βChloroβnitrosobutane.

Solvent.	Dark.	Light.	Difference.
Methyl Alcohol.	292	49	243
Methyl Alcohol.	292	48	244
Acetone.	292	92	200
Acetone.	292	95	197
Unexposed Alcohol.	292	190	102
Unexposed Acetone.	292	195	97
Unexposed Alcohol diluted to 0·6 orig.	292	73	219
Unexposed Acetone diluted to 0·6 orig.	292	79	213

----------oOo----------

TABLE 23.

Effect of Solvent on Quantum Yield of βChloroβnitrosobutane.

Solvent.	Dark.	Light.	Difference.
Methyl Alcohol.	293	161	132
Methyl Alcohol.	293	162	131
Dioxan.	293	176	117
Dioxan.	293	176	117
Unexposed Alcohol.	293	192	101
Unexposed Dioxan.	293	198	95
Unexposed Alcohol diluted to 0·8 orig.	293	139	154
Unexposed Dioxan diluted to 0·8 orig.	293	146	147

----------oOo----------

where oxygen is present, the reaction proceeds differently, different products being obtained.

In Part 2 of this thesis I have described the product of the photo-oxidation of βchloroβnitrosobutane. It was not found possible to measure the quantum yield of the photo-oxidation, as both the photo-oxidation and the decomposition without oxygen proceeded side by side, and even with the most vigourous shaking with oxygen, only about 50% of the compound was photo-oxidised. Further, no satisfactory method of telling how much was decomposed by oxidation could be found. The amount of oxygen absorbed was useless, as it was not theoretical, and continued after the illumination was stopped. It was at first thought that the amount of HCl set free might give a measure of the amount decomposed without oxygen, but since the compound absorbed more oxygen than that required to give the chloronitro compound, it is possible that some HCl is also set free in the photo-oxidation. Indeed, traces of HCl were detected when some chloronitrobutane was shaken for several hours with oxygen.

<u>βChloroβnitrosopropane.</u>

No measurements of the quantum yield were carried out with chloronitrosopropane, as the compound was extremely volatile, and it was felt that accurate measurements would not be possible.

TABLE 24.

Quantum Yield of βChloroβnitrosohexane. (Method 2).

Alcohol freed from Oxygen. Concentration 4%.

Conc. gms/100ccs.	0·80	0·72	0·64	0·56	Expt.
Photocell defl. with Proj.Lamp(mm).	146	174	294	238	194

From graph expt. conc. 3·325gms/100ccs.

Initial concentration. 4·000gms/100ccs.

Volume of solution used. 2·7ccs.

Gm. molecules decomposed. $1{\cdot}22 \times 10^{-4}$

Carbon.	1	2	3	4	5	6	7	8	9	10	Av.
Av.Photocell deflection(mm).	116	111	115	117	119	117	118	116	117	118	116

Ratio Thermopile defl./Photo-cell defl. 4·000

Deflection on thermopile with Hefner Lamp. 55·0mm.

Energy absorbed. 4·305 cals.

Quantum Yield. 1·23

TABLE 25.

Quantum Yield of βChloroβnitrosohexane. (Method 2).

Alcohol freed from Oxygen. Concentration 5gms/100gms.

Conc. gms/100gms.	1·001	0·8796	0·7650	0·6241	Expt.
Photocell defl. with Proj.Lamp(mm).	133	163	194	249	176

From graph expt. conc. 4·131gms/100gms.

Initial concentration. 5·075gms/100gms.

Gm. molecules decomposed. $1·346 \times 10^{-4}$

Carbon.	1	2	3	4	5	6	7	8	9	10	Av.
Av.Photocell deflection(mm).	143	136	136	138	130	135	131	128	128	127	133

Ratio Thermopile defl./Photo-cell defl. 3·751

Deflection on thermopile with Hefner Lamp. 55·0mm.

Energy absorbed. 4·63 cals.

Quantum Yield. 1·24

βChloroβnitrosohexane.

The quantum yield for the decomposition of chloronitrosohexane by red light in the absence of air was measured by the same method as for chloronitrosobutane. (Method 2). Since the head of the band is at 6530A, the Christiansen filter was kept at 15·4°C to give light of that wave-length. The solution used was a 4% solution in methyl alcohol. The values obtained (Tables 24 and 25) are practically identical with the corresponding values for chloronitrosobutane. It thus seems certain that the quantum yield is 1 for this compound as well.

The quantum yield for the photo-oxidation could not be measured, as no means of differentiating between the decomposition with oxygen and that without oxygen could be obtained.

SUMMARY.

In this thesis I have described the photo-chemical decomposition of βchloroβnitrosopropane, βchloroβnitrosobutane and βchloroβnitrosohexane both in the presence and in the absence of oxygen.

In the decomposition of βchloroβnitrosobutane in the absence of oxygen, the products isolated were:-
(1) HCl, (2) methyl ethyl ketoxime, (3) diacetyl monoxime, (4) γhydroxyγδdimethylhexanβεdionedioxime and (5) the monohydrochloride of γδdimethylΔγhexadieneβεdionedioxime.

It was also shown that (4) was obtained from (5) by the addition of water and neutralisation. Further, (2) and (3) were obtained when (4) was allowed to stand in alcoholic HCl.

In the case of βchloroβnitrosopropane, the compounds isolated were HCl, acetoxime and the monoxime of the ketonic aldehyde CH_3COCHO. In the case of βchloroβnitrosohexane, methyl butyl ketoxime and the monoxime of 2-3-diketohexane were detected in addition to HCl. In both cases the double molecules corresponding to (4) and (5) could not be isolated.

The following mechanism has been suggested for the decomposition in the absence of air. X and Y are alkyl radicals.

$$X-\overset{NO}{\underset{Cl}{C}}-CH_2-Y + h\nu = X-\overset{NO}{C}=CH-Y + HCl$$

$$2\ X-\overset{NO}{C}=CH-Y + HCl = X-\overset{HON}{C}-\overset{Y}{C}=\overset{Y}{C}-\overset{NOH.HCl}{C}-X$$

$$X-\overset{HON}{C}-\overset{Y}{C}=\overset{Y}{C}-\overset{NOH.HCl}{C}-X + H_2O + KOH = X-\overset{HON}{C}-\overset{Y}{COH}-\overset{Y}{CH}-\overset{NOH}{C}-X + KCl$$

$$X-\overset{HON}{C}-\overset{Y}{COH}-\overset{Y}{CH}-\overset{NOH}{C}-X + \text{alc. } HCl = X-\overset{NOH}{C}-CO-Y + X-\overset{NOH}{C}-CH_2-Y$$

In the decomposition in the presence of oxygen, two reactions occurred, the one above and the photo-oxidation. In each case the product isolated was the corresponding chloronitro compound. The fact that the oxidation did not stop at that stage, but proceeded further was proved

by the following facts.

(1) The amount of oxygen absorbed was 2-3 times the theoretical amount.

(2) Absorption of oxygen continued in the dark after a period of illumination.

(3) Traces of the oxy-acids of nitrogen were detected in the solution.

In the third part of the thesis there is described the method evolved for the measurement of quantum yields with red light. Noteworthy features of the method are the use of the carbon arc as the light source, with a photo-electric cell and a recording galvanometer to record variations in intensity; the use of the Christiansen filter to obtain monochromatic light, and the use of a constant light source and a photo-cell to measure the change in concentration.

The quantum yield for the photolysis of β-chloro-β-nitrosobutane and β-chloro-β-nitrosohexane in methyl alcohol was measured and found to be 1·2 in each case. Additional experiments showed that in the case of chloronitrosobutane, the quantum yield is independent of concentration between 2% and 8%. It was also shown that the quantum yield was not affected by the presence of HCl, but was greater when oxygen was present and smaller when acetone or dioxan was used as solvent.

The absorption spectra of the three chloronitroso

compounds studied were measured with a Goldberg Spectrodensograph. They all showed the characteristic unsymmetrical band in the red associated with the NO group.

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